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"Nec aranearum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit.* lib. i. cap. 1. Not.

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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua .... Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

——" Cur spirent venti, cur terra dehiscat,
Cur mare turgescat, pelago cur tantus amaror,
Cur caput obscura Phœbus ferrugine condat,
Quid toties diros cogat flagrare cometas,
Quid pariat nubes, veniant cur fulmina cœlo,
Quo micet igne Iris, superos quis conciat orbes
Tam vario motu."

J. B. Pinelli ad Mazonium.

ALERE FLAMMAM.

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[SIXTH SERIES.]

JANUARY 1922.

I. *Zonal Harmonics of the Second Type.*

By J. W. NICHOLSON, *F.R.S.*[*]

THE function $Q_n(\mu)$ has received but little study in some of its aspects. In fact, nowhere in the literature of the subject has the writer been able to find the value of the integral

$$\int_{-1}^{1}[Q_n(\mu)]^2 d\mu,$$

which is clearly fundamental. Together with certain other properties of the function, it was found necessary recently to evaluate this integral in connexion with the solution of an integral equation arising in the problem of two parallel conducting disks. The capacity of an electrical condenser of this type depends on these properties, and can be expressed without approximation as an integral containing Q functions. A short account of these properties which, though apparently not on record or perhaps unknown, can be obtained in an elementary way, is given in the present note.

The function $Q_n(\mu)$, the second solution of Legendre's equation, may be defined by

$$Q_n(\mu)=\tfrac{1}{2}P_n(\mu)\log\frac{1+\mu}{1-\mu}-\sum_{r=0} a_r P_{n-2r-1}$$

when μ is less than unity, where the coefficients a_r are numerical.

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[*] Communicated by the Author.

In the first place, by a usual procedure in the theory of differential equations, we can show at once that

$$(m-n)(m+n+1)\int_{-1}^{1} Q_m(\mu)\, Q_n(\mu)\, d\mu$$
$$=\left[(1-\mu^2)(Q_m Q_n'-Q_n Q_m')\right]_{-1}^{1},$$

the accent denoting differentiation with respect to μ. We shall suppose throughout that m and n are integers, and that μ lies between the values ± 1.

The right-hand side of this equation becomes, by an easy reduction,

$$(1-\mu^2)\sum_{r=0} a_r P_{n-2r-1} \sum_{s=0} a_s P'_{n-2s-1} - (1-\mu^2)\sum a_r P'_{n-2r-1} \sum a_s P_{n-2s-1}$$
$$-\tfrac{1}{2}(1-\mu^2) P_n' \log\frac{1+\mu}{1-\mu} \sum a_r P_{m-2r-1} + \tfrac{1}{2}(1-\mu^2) P_m' \log\frac{1+\mu}{1-\mu} \sum a_s P_{n-2s-1}.$$

The functions P and P′ are polynomials, and finite for all the values of μ concerned. Thus the first row vanishes by virtue of its factor $1-\mu^2$. The second also vanishes because the limit of

$$(1-\mu^2)\log\frac{1+\mu}{1-\mu}$$

is zero when $\mu=\pm 1$. We deduce that

$$(m-n)(m+n+1)\int_{-1}^{1} Q_m Q_n\, d\mu = 0,$$

and if m and n are different,

$$\int_{-1}^{1} Q_m Q_n\, d\mu = 0. \qquad \ldots \ldots \quad (1)$$

It is more difficult to discuss the case $m=n$. The generating function f of the series

$$\Sigma_0^\infty h^n Q_n(\mu) = f(\mu, h),$$

which also defines $Q_n(\mu)$ when n is an integer, is too complicated to permit of use after the usual manner adopted for the zonal harmonic P_n. Instead, we shall expand $Q_n(\mu)$ in a series of harmonics of type $P_n(\mu)$. The possibility of the expansion is evident from the facts that (1) the product $P_p(\mu)\, P_q(\mu)$ is so expansible by Adams's theorem, and (2) $\log\frac{1+\mu}{1-\mu}$, except at $\mu=\pm 1$, must admit such an expansion because the integral

$$\int_{-1}^{1} P_n(\mu) \log\frac{1+\mu}{1-\mu}\,d\mu$$

exists, and in fact can be determined readily.

For we know that if p is any integer,

$$\int_{-1}^{1} P_p(\mu)\,d\mu = 0.$$

Moreover,

$$\int_{-1}^{1} Q_n(\mu)\,d\mu = -\left[\frac{1}{n(n+1)}\cdot(1-\mu^2)\frac{dQ_n}{d\mu}\right]_{-1}^{1}.$$

Near $\mu = \pm 1$, $\frac{dQ_n}{d\mu}$ is infinite like $\frac{P_n(\mu)}{1-\mu^2}$ or like $\frac{P_n(1)}{1-\mu^2}$.

Thus

$$\int_{-1}^{1} Q_n(\mu)\,d\mu = -\frac{1-(-)^n}{n(n+1)} = 0 \quad \text{if } n \text{ is even,}$$

$$= \frac{-2}{n(n+1)} \quad \text{if } n \text{ is odd.}$$

Accordingly, reverting to the definition of Q_n,

$$\int_{-1}^{1} P_n(\mu) \log\frac{1+\mu}{1-\mu}\,d\mu = \frac{-4}{n(n+1)} \quad \text{if } n \text{ is odd,}$$

$$= 0 \quad \text{if } n \text{ is even.}$$

This is equivalent to

$$\int_{-1}^{1} P_n(\mu)\,Q_0(\mu)\,d\mu = \frac{-2}{n(n+1)} \quad \text{or zero,}$$

and enables us to write down the expansion of $Q_0(\mu)$ at once in the form

$$-Q_0(\mu) = \frac{3}{1\,.\,2}P_1(\mu) + \frac{7}{3\,.\,4}P_3(\mu) + \frac{11}{5\,.\,6}P_5(\mu) + \ldots . \qquad (2)$$

This result is quite elementary. For the general expansion, we return to the differential equation, and can show readily that

$$(m-n)(m+n+1)\int_{-1}^{1} P_n(\mu)\,Q_m(\mu)\,d\mu$$

$$= \Big[(1-\mu^2)(Q_m P_n' - P_n Q_m')\Big]_{-1}^{1}, \qquad (3)$$

where the only terms in the bracket, not obviously zero as polynomials with factor $1-\mu^2$, are

$$\tfrac{1}{2}(1-\mu^2)\mathrm{P}_m\mathrm{P}_n'\log\frac{1+\mu}{1-\mu}-\tfrac{1}{2}(1-\mu^2)\mathrm{P}_n\mathrm{P}_m'\log\frac{1+\mu}{1-\mu}$$
$$-\tfrac{1}{2}\mathrm{P}_m\mathrm{P}_n(1-\mu^2)\frac{d}{d\mu}\log\frac{1+\mu}{1-\mu}.$$

The first and second of these three expressions tend to zero at the limits, and thus

$$(m-n)(m+n+1)\int_{-1}^{1}\mathrm{P}_n(\mu)\,\mathrm{Q}_m(\mu)\,d\mu=-\Big[\mathrm{P}_m\mathrm{P}_n\Big]_{-1}^{1}$$
$$=(-)^{m+n}-1,$$

and is zero if $m+n$ is even, and equal to -2 if $m+n$ is odd.

We deduce the two formulæ

$$\int_{-1}^{1}\mathrm{Q}_{2m}(\mu)\,\mathrm{P}_{2n+1}(\mu)\,d\mu=\frac{-2}{(2m-2n-1)(2m+2n+2)}, \quad (4)$$

$$\int_{-1}^{1}\mathrm{Q}_{2m+1}(\mu)\,\mathrm{P}_{2n}(\mu)\,d\mu=\frac{-2}{(2m-2n+1)(2m+2n+2)}, \quad (5)$$

where m and n are integers. Since when n is odd, Q_n is an even function of μ and P_n an odd function, and *vice versâ*,

$$\int_{-1}^{1}\mathrm{P}_p(\mu)\,\mathrm{Q}_q(\mu)\,d\mu=0 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in all cases in which p and q are both odd or both even.

Similar integrals from *zero* to unity are of importance in the applications mentioned. For these, we require $\mathrm{Q}_n(0)$, $\mathrm{Q}_n'(0)$. Since

$$\mathrm{Q}_n(\mu)=\tfrac{1}{2}\mathrm{P}_n\log\frac{1+\mu}{1-\mu}-\left\{\frac{2n-1}{1\,.\,n}\mathrm{P}_{n-1}+\frac{2n-5}{3\,.\,n-1}\mathrm{P}_{n-3}+\ldots\right\}, \quad . \quad . \quad . \quad (7)$$

we readily find

$$\mathrm{Q}_0(0)=0,\quad \mathrm{Q}_1(0)=-1,\quad \mathrm{Q}_2(0)=\tfrac{2}{3},\quad \mathrm{Q}_3(0)=-\tfrac{8}{15},$$

corresponding to

$$\mathrm{P}_0(0)=1,\quad \mathrm{P}_1(0)=0,\quad \mathrm{P}_2(0)=-\tfrac{1}{2},\quad \mathrm{P}_3(0)=0.$$

The values of $\mathrm{P}_n'(0)$ are coefficients of powers of h in the expansion of $h(1+h^2)^{-3/2}$, the general value being

$$\mathrm{P}'_{2n}(0)=0,\qquad \mathrm{P}'_{2n+1}(0)=(-)^n\,.\,\frac{3\,.\,5\,.\,7\ldots 2n+1}{2\,.\,4\,.\,\ldots 2n}, \quad (8)$$

as against

$$P_{2n+1}(0)=0, \qquad P_{2n}(0)=(-)^n\frac{1.3.\ldots 2n-1}{2.4.\ldots 2n}. \quad (9)$$

The Q's admit a recurrence formula

$$(n+1)\,Q_{n+1}-(2n+1)\,\mu\,Q_n+n\,Q_{n-1}=0,$$

so that $Q_{n+1}(0)\,/\,Q_{n-1}(0)=-n\,/\,(n+1)$

or $Q_{n+2}(0)\,/\,Q_n(0)=-(n+1)\,/\,(n+2).$

We thus find without difficulty, that

$$Q_{2n}(0)=0, \qquad Q_{2n+1}(0)=(-)^n\cdot\frac{2.4.\ldots 2n}{3.5.\ldots 2n+1}. \quad (10)$$

From another recurrence formula,

$$(2n+1)\,\mu\,Q_n'=(n+1)\,Q'_{n-1}+n\,Q'_{n+1},$$

we have $Q'_{n+1}(0)\,/\,Q'_{n-1}(0)=-(n+1)\,/\,n$

or $Q'_{n+2}(0)\,/\,Q_n'(0)=-(n+2)\,/\,(n+1).$

But $Q_0'(\mu)=\dfrac{1}{1-\mu^2}, \qquad Q_0'(0)=1,$

whence $Q_1'(0)=0,$

$$Q'_{2n+1}(0)=0, \qquad Q'_{2n}(0)=(-)^n\frac{2.4.\ldots 2n}{1.3.\ldots 2n-1}. \quad (11)$$

Returning to the formula

$$(m-n)(m+n+1)\int P_n\,Q_m\,d\mu=(1-\mu^2)(Q_m P_n'-P_n Q_m'),$$

which is true between any two limits, we can evaluate the whole set of integrals between limits zero and unity. Thus

$$\begin{aligned}(2m-2n)(2m+2n+1)&\int_0^1 P_{2n}Q_{2m}\,d\mu\\ &=-P_{2n}(1)P_{2m}(1)-\{Q_{2m}(0)\,P'_{2n}(0)-P_{2n}(0)\,Q'_{2m}(0)\}\\ &=-1+(-)^{m+n}\frac{1.3.\ldots 2n-1}{2.4.\ldots 2n}\cdot\frac{2.4.\ldots 2m}{1.3.\ldots 2m-1}, \quad (12)\end{aligned}$$

$$\begin{aligned}(2m-2n-1)(2m+2n+2)&\int_0^1 P_{2n+1}Q_{2m}\,d\mu\\ &=-1-\{Q_{2m}(0)\,P'_{2n+1}(0)-P_{2n+1}(0)\,Q'_{2m}(0)\}=-1. \quad (13)\end{aligned}$$

Thus

$$\int_0^1 P_{2n+1}(\mu)\,Q_{2m}(\mu)\,d\mu = -1\,/\,(2m-2n-1)(2m+2n+2) \quad . \;\; . \;\; . \quad (14)$$

for all integer values of m and n. In the same way,

$$\int_0^1 P_{2n}(\mu)\,Q_{2m+1}(\mu)\,d\mu = -1\,/\,(2m-2n+1)(2m+2n+2), \quad . \;\; . \;\; . \quad (15)$$

and the fourth case can be worked out at once.

Expansions of Harmonic Functions.

If, returning to (4), we have

$$Q_{2m}(\mu) = \Sigma_0^\infty a_n P_{2n+1}(\mu).$$

Then

$$a_n \cdot \frac{2}{4n+3} = \int_{-1}^1 Q_{2m}(\mu)\,P_{2n+1}(\mu)\,d\mu$$

$$= -\frac{2}{(2m-2n-1)(2m+2n+2)},$$

and we obtain the expansion

$$Q_{2m}(\mu) = -\sum_{n=0}^{\infty} \frac{(4n+3)\,P_{2n+1}(\mu)}{(2m-2n-1)(2m+2n+2)}, \quad . \quad (16)$$

which is convergent when μ is between ± 1, both exclusive.

Similarly, with the same convergence,

$$Q_{2m+1}(\mu) = -\Sigma_0^\infty \frac{(4n+1)\,P_{2n}(\mu)}{(2m-2n+1)(2m+2n+2)} \; . \; . \quad (17)$$

The same expansions are valid for the "associated Legendre functions"

$$P_m{}^r(\mu), \quad Q_n{}^r(\mu) = (1-\mu^2)^{m/2}\,\frac{d^r}{d\mu^r}\,(P_n,\,Q_n)$$

by operating on both sides. Thus

$$Q_{2m}{}^r(\mu) = -\Sigma_0^\infty \frac{(4n+3)\,P_{2n+1}{}^r(\mu)}{(2m-2n-1)(2m+2n+2)}, \quad . \quad (18)$$

$$Q_{2m+1}{}^r(\mu) = -\Sigma_0^\infty \frac{(4n+1)\,P_{2n}{}^r(\mu)}{(2m-2n+1)(2m+2n+2)} \; . \; . \quad (19)$$

From (16) we obtain, on squaring,

$$\int_{-1}^{1}[\mathrm{Q}_{2m}(\mu)]^2 d\mu$$

$$=\Sigma_0^\infty\frac{(4n+3)^2}{(2m-2n-1)^2(2m+2n+2)^2}\int_{-1}^{1}[\mathrm{P}_{2n+1}(\mu)]^2 d\mu,$$

the limits not requiring delicate considerations. Thus

$$\int_{-1}^{1}[\mathrm{Q}_{2m}(\mu)]^2 d\mu=2\Sigma_0^\infty\frac{4n+3}{(2m-2n-1)^2(2m+2n+2)^2}$$

$$=\frac{2}{4m+1}\Sigma_0^\infty\left\{\frac{1}{(2m-2n-1)^2}-\frac{1}{(2m+2n+2)^2}\right\}. \quad . \quad . \quad . \quad (20)$$

This can be expressed in Gamma functions. For the special case $m=0$, the value is

$$2\left(\frac{1}{1^2}-\frac{1}{2^2}+\frac{1}{3^2}-\frac{1}{4^2}\cdots\right)=\frac{\pi^2}{6}.$$

For $m=1$, it becomes

$$\frac{2}{5}\left\{\frac{1}{1^2}+\frac{1}{1^2}+\frac{1}{3^2}+\frac{1}{5^2}+\cdots-\frac{1}{4^2}-\frac{1}{6^2}-\frac{1}{8^2}\cdots\right\}$$

$$=\frac{2}{5}\left\{1+\frac{\pi^2}{8}-\frac{1}{4}\left(\frac{\pi^2}{6}-1\right)\right\}=\frac{2}{5}\left(\frac{5}{4}+\frac{\pi^2}{12}\right).$$

In general, the value may be written as

$$\frac{2}{4m+1}\left\{\left(\frac{1}{1^2}+\frac{1}{3^2}+\cdots+\frac{1}{(2m-1)^2}\right)+\left(\frac{1}{1^2}+\frac{1}{3^2}+\ldots\text{ ad inf.}\right)\right.$$

$$\left.-\left(\frac{1}{(2m+2)^2}+\frac{1}{(2m+4)^2}+\ldots\text{ ad inf.}\right)\right\},$$

or

$$\frac{2}{4m+1}\left\{2\left(\frac{1}{1^2}+\frac{1}{3^2}+\cdots\right)-\left(\frac{1}{(2m+1)^2}+\frac{1}{(2m+2)^2}+\cdots\right)\right\},$$

or

$$\frac{2}{4m+1}\left\{\frac{\pi^2}{4}+\frac{d^2}{dz^2}\log\Gamma(z)\right\}_{z=2m}.$$

Finally,

$$\int_{-1}^{1}[\mathrm{Q}_{2m}(\mu)]^2 d\mu=\frac{2}{4m+1}\left\{\frac{\pi^2}{4}+\frac{d^2}{dz^2}\log\Gamma(z)\right\}_{z=2m}. \quad (21)$$

By the use of Binet's formula when z is large, we readily find that the second term of the bracket is of order $\frac{1}{m}$ when m is large, so that the integral tends, for large values of m, to $\frac{\pi^2}{8m}$. This is important in regard to the convergency of series of Q functions obtained as representations of given functions.

The case of functions of odd order may be noticed briefly. We show without difficulty that

$$\int_{-1}^{1} [Q_{2m+1}(\mu)]^2 d\mu$$

$$= 2\Sigma_0^\infty \frac{4n+1}{(2m-2n+1)^2(2m+2n+2)^2}$$

$$= \frac{2}{4m+3}\Sigma_0^\infty \left\{\frac{1}{(2m-2n+1)^2} - \frac{1}{(2m+2n+2)^2}\right\}$$

$$= \frac{2}{4m+3}\left\{\left(\frac{1}{1^2}+\frac{1}{3^2}+\ldots+\frac{1}{(2m+1)^2}\right)+\left(\frac{1}{1^2}+\frac{1}{3^2}+\ldots \text{ ad inf.}\right)\right.$$
$$\left.-\left(\frac{1}{(2m+2)^2}+\frac{1}{(2m+4)^2}+\ldots\right)\right\}$$

$$= \frac{2}{4m+3}\left\{\frac{\pi^2}{4} - \frac{1}{(2m+2)^2} - \frac{1}{(2m+3)^2} - \ldots\right\},$$

and finally

$$\int_{-1}^{1} [Q_{2m+1}(\mu)]^2 d\mu = \frac{2}{4m+3}\left\{\frac{\pi^2}{4} + \frac{d^2}{dz^2}\log\Gamma(z)\right\}_{z=2m+1}. \qquad (22)$$

The formulæ are clearly the same whether the order of the function Q be odd or even.

Catalan gave the following expansion :—

$$\sin^{-1}\mu = \frac{\pi}{2}\Sigma_0^\infty\left(\frac{1.3.\ldots 2n-1}{2.4.\ldots 2n}\right)^2\{P_{2n+1}(\mu)-P_{2n-1}(\mu)\},$$

which is typical of other useful results not apparently noticed. If this be differentiated, we find, since

$$\frac{dP_{2n+1}}{d\mu} - \frac{dP_{2n-1}}{d\mu} = (4n+1)P_{2n},$$

that $$\frac{1}{\sqrt{1-\mu^2}} = \frac{\pi}{2}\Sigma_0^\infty(4n+1)\left(\frac{1.3.\ldots.2n-1}{2.4.\ldots.2n}\right)^2 P_{2n}(\mu).$$

The simplest proof is probably by use of the formula

$$\int_0^\pi \mathrm{P}_n(\cos\theta\cos\theta'+\sin\theta\sin\theta'\cos\phi)\,d\phi$$
$$=\pi\,\mathrm{P}_n(\cos\theta)\,\mathrm{P}_n(\cos\theta\,).$$

Writing $\theta=\theta'=\frac{\pi}{2}$,

$$\int_0^\pi \mathrm{P}_n(\cos\phi)\,d\phi=\pi[\mathrm{P}_n(0)]^2,$$

which is zero when n is odd. Writing $\cos\phi=\mu$, we have

$$\int_{-1}^1 \frac{\mathrm{P}_n(\mu)}{\sqrt{1-\mu^2}}\,d\mu=\pi[\mathrm{P}_n(0)]^2,$$

leading immediately to the expansion.

If a direct proof be adopted as follows, we obtain important properties of the Q functions. For, whether P stands for P or Q, we have

$$n(n+1)\int \mathrm{P}_n(\mu)\,d\mu=-\sqrt{1-\mu^2}\frac{d\mathrm{P}_n}{d\mu}+\int\frac{\mu}{\sqrt{1-\mu^2}}\frac{d\mathrm{P}_n}{d\mu}\,d\mu;$$

and therefore, applying this formula twice, if

$$u_n=\int\frac{\mathrm{P}_n(\mu)}{\sqrt{1-\mu^2}}\,d\mu,$$

we have

$$n(n+1)\,u_n-(n-2)(n-1)\,u_{n-2}$$

$$=\int\frac{\mu}{\sqrt{1-\mu^2}}\left(\frac{d\mathrm{P}_n}{d\mu}-\frac{d\mathrm{P}_{n-2}}{d\mu}\right)d\mu-\sqrt{1-\mu^2}\left(\frac{d\mathrm{P}_n}{d\mu}-\frac{d\mathrm{P}_{n-2}}{d\mu}\right)$$

$$=-(2n-1)\sqrt{1-\mu^2}\,\mathrm{P}_{n-1}+(2n-1)\int\frac{\mu\,\mathrm{P}_{n-1}}{\sqrt{1-\mu^2}}\,d\mu$$

$$=-(2n-1)\sqrt{1-\mu^2}\,.\,\mathrm{P}_{n-1}+n\,u_n+(n-1)u_{n-2}$$

or $\quad n^2u_n-(n-1)^2u_{n-2}=-(2n-1)\sqrt{1-\mu^2}\,\mathrm{P}_{n-1}.$

Between limits ±1, the right side vanishes whether the P or Q function is concerned, and

$$u_n/u_{n-2}=(n-1/n)^2.$$

Thus

$$\int_{-1}^{1}\frac{P_{2n}(\mu)}{\sqrt{1-\mu^2}}d\mu=\left(\frac{1.3.\ldots 2n-1}{2.4.\ldots 2n}\right)^2\int_{-1}^{1}\frac{d\mu}{\sqrt{1-\mu^2}},$$

leading at once to the result. Moreover,

$$\int_{-1}^{1}\frac{Q_{2n+1}(\mu)}{\sqrt{1-\mu^2}}d\mu=\left(\frac{2.4.\ldots 2n}{3.5.\ldots 2n+1}\right)^2\int_{-1}^{1}\frac{Q_1(\mu)}{\sqrt{1-\mu^2}}d\mu. \quad (23)$$

The last integral is readily evaluated. For

$$Q_1(\mu)=\tfrac{1}{2}\mu\log\frac{1+\mu}{1-\mu}-1,$$

and therefore

$$\int_{-1}^{1}\frac{Q_1(\mu)}{\sqrt{1-\mu^2}}d\mu=\int_0^{\pi}\left(\tfrac{1}{2}\cos\theta\log\frac{1+\cos\theta}{1-\cos\theta}-1\right)d\theta$$

$$=\int_0^{\pi}\cos\theta\log\cot\frac{\theta}{2}d\theta-\pi$$

$$=2\int_0^{\pi/2}\cos 2\theta\,(\log\cos\theta-\log\sin\theta)\,d\theta-\pi.$$

Now when r is odd, it is known from a familiar result in the integral calculus that

$$\int_0^{\pi/2}\cos 2r\theta\log\cot\theta\,d\theta=\frac{\pi}{2r}.$$

So that, in the present case $r=1$, we find

$$\int_{-1}^{1}\frac{Q_1(\mu)}{\sqrt{1-\mu^2}}d\mu=2\,.\,\frac{\pi}{2}-\pi=0.$$

It follows that for *all* integer values of n,

$$\int_{-1}^{1}\frac{Q_n(\mu)}{\sqrt{1-\mu^2}}d\mu=0, \quad . \quad . \quad . \quad . \quad . \quad (24)$$

a somewhat surprising result, which is a special case of a formula in the next section. It can be expressed also in the form

$$\int_0^{\pi}Q_n(\cos\theta)\,d\theta=0. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Relation to Fourier series.

The Fourier series representing $P_n(\mu)$ is well known, and can be found at once. For $P_n(\cos\theta)$ is the coefficient of h^n in the expansion of

$$(1-2h\mu+h^2)^{-\frac{1}{2}}=(1-he^{i\theta})^{-\frac{1}{2}}(1-he^{-i\theta})^{-\frac{1}{2}}$$

and expanding each bracket and multiplying directly, we find

$$P_n(\cos\theta)=2\,.\,\frac{2n\,!}{2^{2n}(n\,!)^2}\left\{\cos n\theta+\frac{1}{2}\cdot\frac{2n}{2n-1}\cos(n-2)\theta\right.$$
$$\left.+\frac{1\,.\,3}{2\,.\,4}\cdot\frac{2n\,.\,2n-2}{2n-1\,.\,2n-3}\cos(n-4)\theta+\,\ldots\right\}. \quad (26)$$

This involves the fact that

$$\int_0^\pi P_n(\cos\theta)\cos(n-2r)\,\theta\,d\theta$$
$$=\pi\,.\,\frac{2n\,!}{2^{2n}(n\,!)^2}\cdot\frac{2r\,!}{2^{2r}(r\,!)^2}\cdot\frac{2n\,.\,2n-2\,.\,\ldots\,2n-2r+2}{2n-1\,.\,\ldots\,2n-2r+1}\quad . \,(27)$$

when $n-2r$ is a positive or negative integer, the integral being zero otherwise when n and r are separately integers. On reduction, with $n-2r=m$, under these circumstances

$$\int_0^\pi P_n(\cos\theta)\cos m\theta\,d\theta=\frac{\Gamma\left(\frac{n+m+1}{2}\right)\Gamma\left(\frac{n-m+1}{2}\right)}{\Gamma\left(\frac{n+m+2}{2}\right)\Gamma\left(\frac{n-m+2}{2}\right)}. \quad (28)$$

This is the same as the integral

$$\int_{-1}^1 P_n(\mu)\cos(m\cos^{-1}\mu)\frac{d\mu}{\sqrt{1-\mu^2}}.$$

Thus we have

$$\frac{\cos(m\cos^{-1}\mu)}{\sqrt{1-\mu^2}}=\Sigma\,A_nP_n(\mu),$$

where

$$A_n=\frac{2n+1}{2}\int_{-1}^1 P_n(\mu)\cos(m\cos^{-1}\mu)\frac{d\mu}{\sqrt{1-\mu^2}}. \quad (n>m)$$

Let m be even. Then n is even, and writing $2m$, $2n$ for them,

$$\frac{\cos(2m\cos^{-1}\mu)}{\sqrt{1-\mu^2}}=\tfrac{1}{2}\Sigma_m^\infty(4n+1)\frac{\Gamma(n+m+\frac{1}{2})\Gamma(n-m+\frac{1}{2})}{\Gamma(n+m+1)\Gamma(n-m+1)}P_{2n}(\mu). \qquad . \; . \; . \quad (29)$$

The case $m=0$ gives the old expansion for $(1-\mu^2)^{-\frac{1}{2}}$. Integrating between zero and μ,

$$\sin(2m\cos^{-1}\mu)$$
$$=m\Sigma_m^\infty\frac{\Gamma(n+m+\frac{1}{2})\,\Gamma(n-m+\frac{1}{2})}{\Gamma(n+m+1)\,\Gamma(n-m+1)}\left\{P_{2n+1}(\mu)-P_{2n-1}(\mu)\right\}, \qquad . \; . \; . \quad (30)$$

of which the case $m=0$ is Catalan's theorem.

We also have

$$\frac{\cos(2m+1\,.\,\cos^{-1}\mu)}{\sqrt{1-\mu^2}}=A_n\,P_{2n+1}(\mu),$$

where

$$A_n=\frac{4n+3}{2}\int_{-1}^{1}P_{2n+1}(\mu)\cos\{(2m+1)\cos^{-1}\mu\}\frac{d\mu}{\sqrt{1-\mu^2}}$$

$$=\frac{4n+3}{2}\frac{\Gamma(n+m+\frac{3}{2})\,\Gamma(n-m+\frac{1}{2})}{\Gamma(n+m+2)\,\Gamma(n-m+1)},$$

and therefore

$$\frac{\cos(2m+1\,.\,\cos^{-1}\mu)}{\sqrt{1-\mu^2}}$$
$$=\tfrac{1}{2}\Sigma_m^\infty(4n+3)\frac{\Gamma(n+m+\frac{3}{2})\,\Gamma(n-m+\frac{1}{2})}{\Gamma(n+m+2)\,\Gamma(n-m+1)}P_{2n+1}(\mu)$$

and

$$\sin(2m+1\,.\,\cos^{-1}\mu)$$
$$=(m+\tfrac{1}{2})\Sigma_m^\infty\frac{\Gamma(n+m+\frac{3}{2})\,\Gamma(n-m+\frac{1}{2})}{\Gamma(n+m+2)\,\Gamma(n-m+1)}\left\{P_{2n+2}(\mu)-P_{2n}(\mu)\right\}. \qquad . \; . \; . \quad (31)$$

In order to obtain corresponding developments relating to Q functions, we first find the Fourier series by another method. We have

$$\int_0^\pi Q_n(\cos\theta)\{\cos m\theta - \cos(m+2)\theta\}\,d\theta$$

$$= 2\int_0^\pi Q_n(\cos\theta)\sin\theta\sin(m+1)\theta\,d\theta$$

$$= \left[\frac{2\sin(m+1)\theta}{n(n+1)}\sin^2\theta\frac{dQ_n}{d\mu}\right]_0^\pi + \frac{2(m+1)}{n(n+1)}\int_0^\pi \sin\theta\cos(m+1)\theta\frac{dQ_n}{d\theta}\,d\theta$$

$$= \left[\frac{2\sin(m+1)\theta}{n(n+1)}\sin^2\theta\frac{dQ_n}{d\mu} + \frac{2(m+1)}{n(n+1)}\sin\theta\cos(m+1)\theta\,.\,Q_n\right]_0^\pi - \frac{2(m+1)}{n(n+1)}\int_0^\pi\{\cos\theta\cos(m+1)\theta - (m+1)\sin\theta\sin(m+1)\theta\}\,Q_n\,d\theta.$$

The integrated terms vanish. If

$$u_m = \int_0^\pi Q_n(\cos\theta)\cos m\theta\,d\theta \quad . \quad . \quad . \quad (32)$$

(m being an integer), the equation is readily reduced to

$$\frac{u_{m+2}}{u_m} = \frac{(n-m)(n+m+1)}{(n-m-1)(n+m+2)} \quad . \quad . \quad . \quad . \quad (33)$$

In particular, if $m=n$, $u_{m+2}=0$, so that

$$\int_0^\pi Q_n(\cos\theta)\cos(n+2)\theta\,.\,d\theta = 0$$

for all integer values of n. This involves the further consequence that

$$\int_0^\pi Q_n(\cos\theta)\cos(n+2r)\theta\,.\,d\theta = 0$$

if n and r are both positive integers. It is, in fact, odd in $\cos\theta$. Again, if $m=n-1$, $u_m=0$, so that

$$\int_0^\pi Q_n(\cos\theta)\cos(n-1)\theta\,.\,d\theta = 0, \quad . \quad . \quad (34)$$

and since
$$\frac{u_m}{u_{m-2}}=\frac{(n-m+2)(n+m-1)}{(n-m+1)(n+m)},$$
we have
$$u_{m-2}=0=u_{n-3}.$$

Thus
$$\int_0^\pi Q_n(\cos\theta)\cos(n-1-2r)\theta\,.\,d\theta=0 \quad . \quad (35)$$
for integer values of n and r.

Now let n be even, and written as $2n$. If m is also even, and written $2m$,
$$u_{2m}=\int_0^\pi Q_{2n}(\cos\theta)\cos 2m\theta\,d\theta$$
$$=u_{2m-2}\frac{(2n-2m+2)(2n+2m-1)}{(2n-2m+1)(2n+2m)},$$
and so down to u_0, which is zero as might be foreseen, Q_{2n} being odd, and $\cos 2m\theta$ even in μ.

Thus
$$\int_0^\pi Q_{2n}(\cos\theta)\cos 2m\theta\,d\theta=0$$
for all integer values of m and n. Similarly,
$$\int_0^\pi Q_{2n+1}(\cos\theta)\cos(2m+1)\theta\,d\theta=0.$$

The equation (35) has a remarkable consequence. For since
$$\int_0^\pi Q_n(\cos\theta)\cos(n-1-2r)\theta\,d\theta=0,$$
and also, the integrand being an odd function,
$$\int_0^\pi Q_n(\cos\theta)\cos(n-2r)\theta\,d\theta=0,$$
it follows that
$$\int_0^\pi Q_n(\cos\theta)\cos m\theta\,d\theta=0 \quad . \quad . \quad . \quad (36)$$
for *all* cases in which $m<n$. A special case is, of course,
$$\int_0^\pi Q_n(\cos\theta)\,d\theta=\int_{-1}^1\frac{Q_n(\mu)}{\sqrt{1-\mu^2}}\,d\mu=0,$$
already proved, whether n be odd or even.

In obtaining Fourier series for the Q functions, our fundamental integrals are therefore

$$\left.\begin{aligned}&\int_0^\pi Q_{2n}(\cos\theta)\cos(2n+1)\theta\,d\theta\\&\int_0^\pi Q_{2n+1}(\cos\theta)\cos(2n+2)\theta\,d\theta\end{aligned}\right\}; \quad . \quad . \quad (37)$$

and to evaluate these, we need a recurrence formula by which the index of Q can be depressed to zero or unity. This formula, ultimately simple, is not easily found.

Starting with

$$\begin{aligned}\mathrm{I}&\equiv\int_0^\pi\left(\frac{d\,Q_n}{d\theta}-\frac{d\,Q_{n-2}}{d\theta}\right)\sin m\theta\,d\theta\\&=-\int_0^\pi\left(\frac{d\,Q_n}{d\mu}-\frac{d\,Q_{n-2}}{d\mu}\right)\sin\theta\sin m\theta\,d\theta\\&=-(2n-1)\int_0^\pi Q_{n-1}\sin\theta\sin m\theta\,d\theta,\end{aligned}$$

by the properties of Q functions, we also have by parts,

$$\mathrm{I}=\Big[(Q_n-Q_{n-2})\sin m\theta\Big]_0^\pi-\int_0^\pi m(Q_n-Q_{n-2})\cos m\theta\,d\theta,$$

where the part in square brackets is zero.

Thus

$$\int_0^\pi Q_{n-1}\sin\theta\sin m\theta\,d\theta=\frac{m}{2n-1}\int_0^\pi(Q_n-Q_{n-2})\cos m\theta\,d\theta.$$

But also, by a property of Q,

$$\begin{aligned}&\int_0^\pi Q_{n-1}\cos\theta\cos m\theta\,d\theta\\&\qquad=\frac{1}{2n-1}\int_0^\pi(n\,Q_n+n-1\,.\,Q_{n-2})\cos m\theta\,d\theta,\end{aligned}$$

or if

$$u_n=\int_0^\pi Q_n(\cos\theta)\cos m\theta\,d\theta, \quad . \quad . \quad . \quad (38)$$

we have by subtraction and addition

$$\begin{aligned}&\int_0^\pi Q_{n-1}\cos(m+1)\theta\,d\theta\\&\qquad=\frac{1}{2n+1}\left\{(n-m)u_n+(n+m-1)u_{n-2}\right\},\\&\int_0^\pi Q_{n-1}\cos(m-1)\theta\,d\theta\\&\qquad=\frac{1}{2n+1}\left\{(n+m)u_n+(n-m-1)u_{n-2}\right\}.\end{aligned}$$

The ratio of the integrals on the left is already known, and therefore

$$\frac{(m+n)u_n+(n-m-1)u_{n-2}}{(n-m)u_n+(n+m-1)u_{n-2}}=\frac{(n-m-1)(n+m)}{(n+m-1)(n-m)},$$

whence we find on reduction

$$\frac{u_n}{u_{n-2}}=\frac{(n+m-1)(n-m-1)}{(n+m)(n-m)} \quad . \quad . \quad . \quad . \quad (39)$$

Applying this formula of reduction, we can show that

$$\int_0^\pi Q_{2n+1}(\cos\theta)\cos(2n+2)\theta\,d\theta$$
$$=\frac{2.4.6.\dots 2n}{1.3.5.\dots 2n-1}\cdot\frac{2n+4.2n+6.\dots 4n+2}{2n+5.2n+7.\dots 4n+3}$$
$$\times\int_0^\pi Q_1(\cos\theta)\cos(2n+2)\theta\,d\theta.$$

This integral can be reduced by the preceding reduction formula, in which the trigonometric function is depressed. We find

$$\int_0^\pi Q_1(\cos\theta)\cos(2n+2)\theta\,d\theta$$
$$=\frac{1.3.\dots 2n-1}{2.4.\dots 2n}\cdot\frac{4.6.\dots 2n+2}{5.7.\dots 2n+3}\int_0^\pi Q_1(\cos\theta)\cos 2\theta\,d\theta,$$

and, finally, the simple form

$$\int_0^\pi Q_{2n+1}(\cos\theta)\cos(2n+2)\theta\,d\theta$$
$$=\frac{4.6.\dots 4n+2}{5.7.\dots 4n+3}\int_0^\pi Q_1(\cos\theta)\cos 2\theta\,d\theta. \quad . \quad (40)$$

Now

$$\int_0^\pi Q_1(\cos\theta)\cos 2\theta\,d\theta$$
$$=\int_0^\pi\left\{\frac{1}{2}\cos\theta\cos 2\theta\log\cot^2\frac{\theta}{2}-\cos 2\theta\right\}d\theta$$
$$=\int_0^{\pi/2}(\cos 2\phi+\cos 6\phi)(\log\cos\phi-\log\sin\phi)d\phi. \quad (\theta=2\phi).$$

Now, if r is odd,

$$\int_0^{\pi/2} \cos 2r\phi\,(\log\cos\phi - \log\sin\phi)\,d\phi = \frac{\pi}{2r}$$

by a well-known formula, and we find

$$\int_0^{\pi} \mathrm{Q}_1(\cos\theta)\cos 2\theta\,d\theta = \frac{\pi}{2} + \frac{\pi}{6} = \frac{2}{3}\pi,$$

or finally,

$$\left.\begin{aligned}\int_0^{\pi} \mathrm{Q}_{2n+1}(\cos\theta)\cos(2n+2)\,\theta\,d\theta &= \pi\,.\frac{2\,.\,4\,.\,\ldots\,4n+2}{3\,.\,5\,.\,\ldots\,4n+3}\\ &= \pi\,.\,2^{4n+2}\frac{(2n+1\,!)^2}{(4n+3\,!)}\end{aligned}\right\}. \quad (41)$$

By applying the reduction formula for the trigonometric function, we also have

$$\mathrm{I}_r \equiv \int_0^{\pi} \mathrm{Q}_{2n+1}(\cos\theta)\cos(2n+2+2r)\,\theta\,d\theta$$

$$= \frac{1\,.\,3\,.\,\ldots\,2r-1}{2\,.\,4\,.\,\ldots\,2r}\,.\,\frac{4n+4\,.\,4n+6\,.\,\ldots\,4n+2r+2}{4n+5\,.\,\ldots\,4n+2r+3}\mathrm{I}_0\,;$$

so that

$$\int_0^{\pi} \mathrm{Q}_{2n+1}(\cos\theta)\cos(2n+2+2r)\,\theta\,d\theta$$

$$= \pi\,.\frac{2r\,!}{(r\,!)^2}\,.\,\frac{(2n+r+1\,!)^2}{(4n+2r+3)\,!}\,.\,2^{4n+2}. \quad (42)$$

Accordingly, between zero and π, Q_{2n+1} admits the Fourier series

$$\mathrm{Q}_{2n+1}(\cos\theta)$$

$$= 2^{4n+3}\frac{(2n+1\,!)^2}{4n+3\,!}\Big\{\cos(2n+2)\,\theta + \frac{1}{2}\,.\,\frac{4n+4}{4n+5}\cos(2n+4\theta)$$

$$+ \frac{1\,.\,3}{2\,.\,4}\,.\,\frac{4n+4\,.\,4n+6}{4n+5\,.\,4n+7}\,.\cos(2n+6)\,\theta + \ldots\Big\}, \quad (43)$$

which ceases to converge at the limits.

We now consider the integral

$$\int_0^{\pi} \mathrm{Q}_{2n}(\cos\theta)\cos(2n+1)\,\theta\,d\theta.$$

This, by successive reduction of the order of Q, is equivalent to

$$\frac{2 \,.\, 4 \ldots 2n}{1 \,.\, 3 \ldots 2n-1} \cdot \frac{2n+2 \,.\, 2n+4 \ldots 4n}{2n+3 \ldots 4n+1} \int_0^\pi \mathrm{Q}_0(\cos\theta)\cos(2n+1)\theta\, d\theta.$$

By the other reduction formula, we find

$$\int_0^\pi \mathrm{Q}_0(\cos\theta)\cos(2n+1)\theta\, d\theta = \frac{1 \,.\, 3 \ldots 2n-1}{2 \,.\, 4 \ldots 2n} \cdot \frac{2 \,.\, 4 \ldots 2n}{3 \,.\, 5 \ldots 2n+1} \int \mathrm{Q}_0(\cos\theta)\cos\theta\, d\theta$$

and therefore

$$\int_0^\pi \mathrm{Q}_{2n}(\cos\theta)\cos(2n+1)\theta\, d\theta \quad \frac{2 \,.\, 4 \ldots 4n}{3 \,.\, 5 \ldots 4n+1} \int_0^\pi \mathrm{Q}_0(\cos\theta)\cos\theta\, d\theta.$$

The last integral is

$$\int_0^\pi \frac{1}{2}\cos\theta \log\cot^2\frac{\theta}{2}\, d\theta = 2\int_0^{\pi/2} \cos 2\phi \log\cot\phi\, d\phi = \pi,$$

and thus

$$\int_0^\pi \mathrm{Q}_{2n}(\cos\theta)\cos(2n+1)\theta\, d\theta = \pi \,.\, 2^{4n}\frac{(2n\,!)^2}{4n+1\,!}. \qquad (44)$$

Moreover,

$$\int_0^\pi \mathrm{Q}_{2n}(\cos\theta)\cos(2n+1+2r)\theta\, d\theta = \frac{1 \,.\, 3 \ldots 2r-1}{2 \,.\, 4 \ldots 2r} \, \frac{4n+2 \,.\, 4n+4 \ldots 4n+2r}{4n+3 \ldots 4n+2r+1} \times \int_0^\pi \mathrm{Q}_{2n}\cos(2n+1)\theta\, d\theta,$$

whence

$$\int_0^\pi \mathrm{Q}_{2n}(\cos\theta)\cos(2n+1+2r)\theta\, d\theta = \pi\frac{2r\,!}{(r\,!)^2}\,\frac{(2n+r\,!)^2}{4n+2r+1\,!} \cdot 2^{4n}, \qquad \ldots \quad (45)$$

the corresponding Fourier series being

$$
\begin{aligned}
&Q_{2n}(\cos\theta)\\
&=2^{4n+1}\frac{(2n\,!)^2}{4n+1\,!}\left\{\cos(2n+1)\theta+\frac{1}{2}\cdot\frac{4n+2}{4n+3}\cos(2n+3)\theta\right.\\
&\qquad\left.+\frac{1\,.\,3}{2\,.\,4}\cdot\frac{4n+2\,.\,4n+4}{4n+3\,.\,4n+5}\cos(2n+5)\theta+\ldots\right\}. \qquad (46)
\end{aligned}
$$

Both series can be combined into the single formula, whether n be odd or even,

$$
\begin{aligned}
&Q_{n}(\cos\theta)\\
&=2^{2n+1}\frac{(n\,!)}{2n+1\,!}\left\{\cos(n+1)\theta+\frac{1}{2}\cdot\frac{2n+2}{2n+3}\cos(n+3)\theta\right.\\
&\qquad\left.+\frac{1\,.\,3}{2\,.\,4}\cdot\frac{2n+2\,.\,2n+4}{2n+3\,.\,2n+5}\cos(n+5)\theta+\ldots\right\}. \qquad (47)
\end{aligned}
$$

The limitation of θ between 0 and π is clearly not necessary.

II. *The Derivation of Symmetrical Gravitational Fields. By* F. D. MURNAGHAN, *Ph.D., Assoc. Prof. Applied Math., Johns Hopkins University* [*].

IN a recent issue of the Philosophical Magazine, Hill and Jeffery [†] call attention to a symmetrical gravitational field which differs somewhat from the classical one due to Schwarzschild and Einstein. In the usual treatment of this problem a field is said to be symmetrical about a point if the form for $(ds)^2$ is invariant under linear orthogonal transformations of the "Cartesian coordinates" (x_1, x_2, x_3); then a transformation is made to "polar coordinates" r, θ, ϕ, where $r=\sqrt{x_1^2+x_2^2+x_3^2}$ etc. and an appeal is made, in choosing a form for $(ds)^2$, to the corresponding form in Euclidean space. Now the essential assumption in the relativity theory of a permanent gravitational field is that the physical space-time continuum of four dimensions is *non*-Euclidean; the term "Cartesian coordinates" for a non-Euclidean space requires definition, and the equation for r given above assumes an underlying

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[*] Communicated by Prof. J. S. Ames.

[†] Phil. Mag. May 1921. The result of this paper has already appeared in a paper by Weyl, *Ann. der Physik,* liv. p. 132 (1917).

Pythagorean theory that is not tenable for non-Euclidean spaces in general. Since the only existing experimental verifications of the relativity *gravitational theory* are based on the expression for $(ds)^2$ in a permanent symmetrical gravitational field, it is desirable that the assumptions in the mathematical treatment should be clearly stated. In the following discussion Einstein and Schwarzschild's form as well as others are derived on certain definitely stated assumptions as to the meaning of the term symmetry, and, peculiarly enough, the differential equations of the theory prove easily integrable, without making any use of the form of the Euclidean element of length on the unit sphere.

According to Einstein the fundamental space which has physical reality (that is, with reference to which the laws of physics must have the tensor form) is of four dimensions. All coordinate systems are, without doubt, equally valid for the description of physical phenomena, but it is reasonable to suppose that for a given observer a certain coordinate system may have a direct and simple relationship to the measurements he makes; such a system is termed a *natural* coordinate system for that observer. For the problem under discussion, one of the natural coordinates x_4 is a *time* coordinate which is such that the coefficients g_{14}, g_{24}, g_{34} in the expression for $(ds)^2$, $(ds)^2 \equiv g_{rs}\,dx_r\,dx_s \ldots$ (r, s umbral or summation symbols) vanish identically whilst the other coefficients g_{rs} do not involve x_4. Accordingly $(ds)^2 \equiv g_{rs}\,dx_r\,dx_s + g_{44}(dx_4)^2 \ldots$ $(r, s = 1, 2, 3)$. Now in a space of three dimensions we can always find an orthogonal system of coordinates (y_1, y_2, y_3) say, for we have merely three differential equations $g^{rs}\frac{\partial y_l}{\partial x_r}\frac{\partial y_m}{\partial x_s} \equiv 0 \ldots$ (r, $s = 1, 2, 3$ are umbral symbols whilst l and m are different numbers of the set 1, 2, 3) (the g^{rs} being the coefficients of the reciprocal form for $(ds)^2$) for the three unknown functions y_1, y_2, y_3 of x_1, x_2, x_3. Hence, using these coordinates instead of x_1, x_2, x_3 (but keeping the notation x instead of y) we see that there is no lack of generality in writing $(ds)^2 \equiv g_{11}(dx_1)^2 + g_{22}(dx_2)^2 + g_{33}(dx_3)^2 + g_{44}(dx_4)^2$, where the coefficients g_{rr} are functions of (x_1, x_2, x_3) at most. [It will be observed in passing that this statical field is very special; it is not in general possible to find orthogonal coordinates in space of four dimensions, there being ***six*** equations $g^{rs}\frac{\partial y_l}{\partial x_r}\frac{\partial y_m}{\partial x_s} = 0 \ldots (r, s = 1, \ldots 4)$ for the four unknown functions y, and these equations are not in general consistent.] It will be convenient to drop the double label, which is now useless, and so we write

$$(ds)^2 \equiv g_1(dx_1)^2 + g_2(dx_2)^2 + g_3(dx_3)^2 + g_4(dx_4)^2.$$

Since $g_{rs} \equiv 0$ if $r \neq s$ the Riemann-Christoffel symbols take comparatively simple forms. If r, s, t are distinct numbers of the set 1, 2, 3, 4,

$$[rs, t] \equiv \frac{1}{2}\left(\frac{\partial g_{rt}}{\partial x_s} + \frac{\partial g_{st}}{\partial x_r} - \frac{\partial g_{rs}}{\partial x_t}\right) \equiv 0$$

and

$$\{rs, t\} \equiv g^{tk}[rs, k] \equiv g^{tt}[rs, t] \equiv 0,$$

since $g^{tk} \equiv 0$ if the umbral symbol k is different from t.

$$\{rs, r\} \equiv \{sr, r\} \equiv g^{rk}[rs, k] \equiv g^{rr}[rs, r] \equiv \frac{1}{2g_r}\frac{\partial g_r}{\partial x_s},$$

since $g^{rr} = \dfrac{1}{g_r}$.

Similarly, $\{rr, r\} \equiv \dfrac{1}{2g_r}\dfrac{\partial g_r}{\partial x_r}$; $\{rr, s\} \equiv -\dfrac{1}{2g_s}\dfrac{\partial g_r}{\partial x_s}$.

The Riemann four-index symbol of the second kind $\{pq, rs\}$ is defined by

$$\{pq, rs\} \equiv \frac{\partial}{\partial x_s}\{pr, q\} - \frac{\partial}{\partial x_r}\{ps, q\}$$
$$+ \{pr, l\}\{ls, q\} - \{ps, l\}\{lr, q\} \ldots$$

(l an umbral symbol).

Hence, if the four letters p, q, r, s have all different numerical values,

$$\{pq, rs\} \equiv 0,$$

since, for example, in the summation $\{pr, l\}\{ls, q\}$ the first factor $\{pr, l\}$ of any term vanishes unless $l = p$ or r, in which cases the second factor vanishes. The remaining types are readily found to be

$$\{pq, qs\} \equiv \frac{1}{2g_q}\frac{\partial^2 g_q}{\partial x_s \partial x_p} - \frac{1}{4g_q^2}\frac{\partial g_q}{\partial x_p}\frac{\partial g_q}{\partial x_s} - \frac{1}{4g_p g_q}\frac{\partial g_p}{\partial x_s}\frac{\partial g_q}{\partial x_p}$$
$$- \frac{1}{4g_s g_q}\frac{\partial g_s}{\partial x_p}\frac{\partial g_q}{\partial x_s},$$

where q is not intended to be an umbral or summation symbol.

$$\{pq, qp\} \equiv \frac{1}{2g_q}\frac{\partial^2 g_q}{\partial x_p{}^2} + \frac{1}{2g_q}\frac{\partial^2 g_p}{\partial x_q{}^2} - \frac{1}{4g_q{}^2}\left(\frac{\partial g_q}{\partial x_p}\right)^2 - \frac{1}{4g_q{}^2}\frac{\partial g_p}{\partial x_q}\frac{\partial g_q}{\partial x_q}$$

$$-\frac{1}{4g_p g_q}\left\{\left(\frac{\partial g_p}{\partial x_q}\right)^2 + \frac{\partial g_p}{\partial x_p}\frac{\partial g_q}{\partial x_p}\right\} + \frac{1}{4g_q}\left\{\frac{1}{g_r}\frac{\partial g_p}{\partial x_r}\frac{\partial g_q}{\partial x_r} + \frac{1}{g_s}\frac{\partial g_p}{\partial x_s}\frac{\partial g_q}{\partial x_s}\right\},$$

where p and q are distinct non-umbral symbols and r, s are different from p and q. In order to obtain the differential equations $G_{rs}=0$, which Einstein assumes the g_r must satisfy, it is necessary to contract this four-index tensor. Thus

$$G_{ps} \equiv \sum_{q=1}^{4}\{pq, qs\} = 0 \quad \text{and} \quad G_{pp} \equiv \sum_{q=1}^{4}\{pq, qp\} = 0$$

are the ten differential equations. Now in the expression for $\{pq, qs\}$ it will be noticed that differentiation with respect to x_s occurs in every term, telling us at once that $\{pq, q4\} \equiv 0$ since none of the coefficients g_r involve x_4. Hence the results

$$G_{14} \equiv 0\,; \quad G_{24} \equiv 0\,; \quad G \equiv 0$$

are a consequence of the assumed properties of a *statical* field.

In the remaining calculations it will simplify matters to observe that in the summation $\sum_{q=1}^{4}\{pq, qs\}$ it is sufficient to give q the two values different from p and s. For, from the definition of the four-index symbols of the *first* kind, $[pp, qs] \equiv 0$ (p not umbral) and, in our system of orthogonal coordinates,

$$\begin{aligned}\{pp, qs\} &\equiv g^{pk}[pk, qs] \ \ldots \ (k \text{ umbral})\\ &\equiv g^{pp}[pp, qs] \equiv 0, \text{ as is similarly } \{pq, ss\}.\end{aligned}$$

(In this argument p, q, s take any numerical values *distinct or not.*) Thus $G_{12} \equiv \{13, 32\} + \{14, 42\}$. We shall now suppose that one set of coordinate lines, x_1 varying say, are geodesics through the space-time point to be specified and the gravitating centre with the same value of x_4, and we may conveniently take x_1 as the arc distance from the gravitating centre, which is, then, a singularity of the coordinate system; for the knowledge of merely two coordinates $x_1=0$ and its x_4 is sufficient to determine it—the other two coordinates x_2 and x_3 being indeterminate (for the sake of an analogy x_1 may be compared with the axial distance in ordinary cylindrical coordinates). The equations of the geodesics in any space are known to be

$\ddot{x}_r + \{lm, r\} \dot{x}_l \dot{x}_m = 0 \ldots (r = 1, \ldots 4\,;\ l, m$ umbral symbols),

dots denoting differentiation with respect to the arc length of the geodesic. Putting x_2, x_3, x_4 all constant, $\dot{x} = 1$, we find

$$\{11, r\} = 0 \ldots (r = 1, 2, 3, 4),$$

yielding $g_1 =$ constant, which constant is in fact unity since $ds = dx_1$ when x_2, x_3, x_4 are constant (by definition of x_1). This argument shows, conversely, that if $g_1 =$ constant the coordinate lines x_1 are geodesics. It is now easily seen that it is sufficient for this that g_1 should be a function of x_1 alone, since a change of coordinates

$$y_1 = \int \sqrt{g_1}\, dx_1\,; \quad y_2 = x_2\,; \quad y_3 = x_3\,; \quad y_4 = x_4$$

leaves the coordinate lines x_1 unaltered. The arc length along these coordinate geodesics is in this case, of course, not x_1 but $\int \sqrt{g_1}\, dx_1$. As an assumption of *symmetry* we now say that g_4 is a function of x_1 alone and not of x_2 nor x_3, and we observe that this together with $g_1 \equiv 1$ makes $\{14, 42\} \equiv 0$, so that

$$\begin{aligned} G_{12} &\equiv \{13, 32\} \\ &= \frac{1}{2g_3} \frac{\partial^2 g_3}{\partial x_1 \partial x_2} - \frac{1}{4{g_3}^2} \frac{\partial g_3}{\partial x_1} \frac{\partial g_3}{\partial x_2} - \frac{1}{4g_2 g_3} \frac{\partial g_2}{\partial x_1} \frac{\partial g_3}{\partial x_2} \\ &= \frac{1}{2} \frac{\partial}{\partial x_1} \left(\frac{1}{g_3} \frac{\partial g_3}{\partial x_2} \right) + \frac{1}{4{g_3}^2} \frac{\partial g_3}{\partial x_1} \frac{\partial g_3}{\partial x_2} - \frac{1}{4g_2 g_3} \frac{\partial g_2}{\partial x_1} \frac{\partial g_3}{\partial x_2}. \end{aligned}$$

Equating this to zero and writing momentarily

$$l_2 \equiv \log g_2\,; \quad l_3 \equiv g_3,$$

it is immediately integrable with respect to x_1 and we have

$$2 \log \frac{\partial l_3}{\partial x_2} + l - l_2 = \text{a function independent of } x_1.$$

The formulæ become more symmetrical from this on if we write $g_r \equiv {H_r}^2$ and express our results in terms of the H_r. Thus the result just obtained may be written

$$\frac{1}{g_2 g_3} \left(\frac{\partial g_3}{\partial x_2} \right)^2 \text{ is independent of } x_1,$$

or equivalently (on extracting the square root)

$$\frac{1}{H_2} \frac{\partial H_3}{\partial x_2} \text{ is independent of } x_1. \quad \ldots \quad \text{(A)}$$

Writing out $G_{11} \equiv \{12, 21\} + \{13, 31\} + \{14, 41\}$ with the simplification $g_1 = 1$, we obtain

$$\frac{1}{2g_2}\frac{\partial^2 g_2}{\partial x_1^2} - \frac{1}{4g_2^2}\left(\frac{\partial g_2}{\partial x_1}\right)^2 + \frac{1}{2g_3}\frac{\partial^2 g_3}{\partial x_1^2} - \frac{1}{4g_3^2}\left(\frac{\partial g_3}{\partial x_1}\right)^2 + \frac{1}{2g_4}\frac{\partial^2 g_4}{\partial x_1^2} - \frac{1}{4g_4}\left(\frac{\partial g_4}{\partial x_1}\right)^2,$$

and on introducing the H_r and equating this to zero there results

$$\frac{1}{H_2}\frac{\partial^2 H_2}{\partial x_1^2} + \frac{1}{H_3}\frac{\partial^2 H_3}{\partial x_1^2} + \frac{1}{H_4}\frac{\partial^2 H_4}{\partial x_1^2} = 0. \quad . \quad . \qquad \text{(B)}$$

The next in simplicity is

$$G_{44} \equiv \{41, 14\} + \{42, 24\} + \{43, 34\}.$$

Remembering that g_4 is a function of x_1 alone and that none of the coefficients involve x_4, we have on equating this to zero

$$\frac{1}{2}\frac{\partial^2 g_4}{\partial x_1^2} - \frac{1}{4g_4}\left(\frac{\partial g_4}{\partial x_1}\right)^2 + \frac{1}{4g_2}\frac{\partial g_4}{\partial x_2}\frac{\partial g_2}{\partial x_1} + \frac{1}{4g_3}\frac{\partial g_4}{\partial x_1}\frac{\partial g_3}{\partial x_1} = 0$$

or

$$H_4\frac{\partial^2 H_4}{\partial x_1^2} + H_4\frac{\partial H_4}{\partial x_1}\left\{\frac{1}{H_2}\frac{\partial H_2}{\partial x_1} + \frac{1}{H_3}\frac{\partial H_3}{\partial x_1}\right\} = 0,$$

which is immediately integrable with respect to x_1, yielding

$$H_2 H_3 \frac{\partial H_4}{\partial x_1} \text{ independent of } x_1. \quad . \quad . \quad . \quad . \qquad \text{(C)}$$

Now the two-dimensional spreads $x_4 = \text{const.}$ $x_1 = \text{const.}$ are what may be termed geodesic spheres. On one of these let us suppose that x_3 is a "longitude" coordinate whilst x_2 is a latitude coordinate. As a demand of symmetry we say that the expression for $(ds)^2$ on this sphere cannot have its coefficients g_2 and g_3 involving the longitude coordinate x_3, whilst the arc differential along a "meridian" curve $ds = \sqrt{g_2}dx_2$ cannot depend on the latitude x_2. Thus g_2 is a function of x_1 alone, whilst g_3 is a function of x_1 and x_2 at most. Just as the non-appearance of the time-coordinate x_4 in the coefficients made $G_{14} = 0$, $G_{24} = 0$, $G_{34} = 0$, so now the absence of x_3 from the coefficients gives in addition $G_{13} = 0$, $G_{23} = 0$. Differentiating

(C) with respect to x_2 and eliminating $\frac{\partial H_3}{\partial x_2}$ by means of (A), we see that $H_2{}^2\frac{\partial H_4}{\partial x_2}$ is independent of x_1; but it cannot involve any of the variables but x_1, since H_2 and H_4 are functions of x_1 alone, and so we conclude that it is a constant.

$$H_2{}^2\frac{\partial H_4}{\partial x_1} = \alpha, \text{ where } \alpha \text{ is an arbitrary constant.} \quad . \quad (C')$$

Let us now write the two remaining equations $G_{22}=0$, $G_{33}=0$. These take relatively simple forms under the hypotheses just made.

$$\begin{aligned} G_{22} &\equiv \{21, 12\} + \{23, 32\} + \{24, 42\} \\ &\equiv \frac{1}{2}\frac{\partial^2 g_2}{\partial x_1{}^2} - \frac{1}{4g_2}\left(\frac{\partial g_2}{\partial x_1}\right)^2 + \frac{1}{2g_3}\frac{\partial^2 g_3}{\partial x_2{}^2} - \frac{1}{4g_3{}^2}\left(\frac{\partial g_3}{\partial x_2}\right)^2 \\ &\qquad + \frac{1}{4g_3}\frac{\partial g_2}{\partial x_1}\frac{\partial g_3}{\partial x_1} + \frac{1}{4g_4}\frac{\partial g_2}{\partial x_1}\frac{\partial g_4}{\partial x_1} \\ &\equiv H_2H_2'' + \frac{1}{H_3}\frac{\partial^2 H_3}{\partial x_2{}^2} + \frac{H_2}{H_3}H_2'\frac{\partial H_3}{\partial x_1} + \frac{H_2}{H_4}H_2'H_4' = 0, \quad (D) \end{aligned}$$

primes denoting as usual differentiations with regard to the argument of the function.

$$\begin{aligned} G_{33} &\equiv \{31, 13\} + \{32, 23\} + \{34, 43\} \\ &\equiv \frac{1}{2}\frac{\partial^2 g_3}{\partial x_1{}^2} - \frac{1}{4g_3}\left(\frac{\partial g_3}{\partial x_1}\right)^2 + \frac{1}{2g_2}\frac{\partial^2 g_3}{\partial x_2{}^2} - \frac{1}{4g_2g_3}\left(\frac{\partial g_3}{\partial x_2}\right)^2 \\ &\qquad + \frac{1}{4g_2}\left(\frac{\partial g_3}{\partial x_1}\right)\left(\frac{\partial g_2}{\partial x_1}\right) + \frac{1}{4g_4}\frac{\partial g_3}{\partial x_1}\frac{\partial g_4}{\partial x_1} \\ &\equiv H_3\frac{\partial^2 H_3}{\partial x_1{}^2} + \frac{H_3}{H_2{}^2}\frac{\partial^2 H_3}{\partial x_2{}^2} + H_3\frac{\partial H_3}{\partial x_1}\left\{\frac{1}{H_2}\frac{\partial H_2}{\partial x_1} + \frac{1}{H_4}\frac{\partial H_4}{\partial x_1}\right\} = 0. \\ &\qquad . \quad . \quad . \quad (E) \end{aligned}$$

Now x_1 and x_2 are the only variables that can enter the coefficients $g_r = H_r{}^2$, so that (A) gives at once $\frac{\partial H_3}{\partial x_2} = H_2\phi'$, where ϕ is a function of x_2 alone, ϕ' being its derivative; whence $H_3 = H_2\phi + f$, where f is a function of x_1 alone. Then (B) shows that $\frac{1}{H_3}\frac{\partial^2 H_3}{\partial x_1{}^2}$ is a function of x_1 alone, so that its derivative with respect to x_2 vanishes identically, yielding

$$\phi'\{fH_2'' - f''H_2\} = 0.$$

Hence either ϕ is a constant, so that all the coefficients depend on x_1 alone, or $fH_2'-f'H_2$ is a constant giving

$$f = \text{constant} \times H_2 \int \frac{dx_1}{H_2^2}.$$

We shall discuss in some detail the case when $f=0$, as this leads immediately to the Einstein-Schwarzschild form. We have

$$H_3 = H_2\phi,$$

and on substituting this in (D) we get

$$H_2H_2''+H_2'^2+H_2H_2'\frac{H_4'}{H_4}+\frac{\phi''}{\phi} = 0.$$

Since the first three terms involve x_1 alone and the last x_2 alone, they must separately be constants which cancel each other. If the constants are zero, we derive $\phi'=$constant. Otherwise, by at most a mere linear transformation on the variable x_2 alone (which is unessential to the argument, since it merely changes the origin of measurement and the size of the unit in which it is measured) we may write

$$\phi = \sin x_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(F)}$$

On substituting $\frac{\phi''}{\phi}=-1$ in the expression just obtained from (D) we find

$$H_2H_2''+H_2H_2'\left\{\frac{H_2'}{H_2}+\frac{H_4'}{H_4}\right\} = 1, \quad . \quad . \quad . \quad \text{(D}'\text{)}$$

and (E) yields exactly the same equation connecting H_2 and H_4. On writing $H_3=H_2 \sin x_2$, (B) becomes

$$2\frac{H_2''}{H_2}+\frac{H_4''}{H_4} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(B}'\text{)}$$

Differentiating (C′) and eliminating H_2H_4'' we obtain

$$H_2''H_4 = H\,'H_4',$$

which yields on integration

$H_2' = \beta H_4$, where β is an arbitrary constant. . (C″)

From (C″) we have

$$H_2'' = \beta H_4' = \frac{\alpha\beta}{H_2^2}. \quad . \quad . \quad . \quad . \quad \text{by (C}'\text{)};$$

$$\therefore \quad H_2'^2 = 2\left(\gamma-\frac{\alpha\beta}{H_2}\right),$$

where γ is an arbitrary constant.

Now on putting $H_4 = \frac{1}{\beta} H_2'$ in (D′) we get

$$2H_2 H_2'' + H_2'^2 = 0,$$

so that $1 = 2\gamma$*, and our solution of the set of differential equations is

$$H_1 = 1\,; \quad H_3 = H_2 \sin x_2\,; \quad H_4 = \frac{1}{\beta} H_2'\,;$$

where H_2 satisfies the simple differential equation

$$H_2'^2 = 1 - \frac{2\alpha\beta}{H_2}.$$

It is now convenient to introduce a new variable r which is a function of x_1 alone, and which is defined in such a way that $H_2 = r$; then

$$dr = \sqrt{1 - \frac{2\alpha\beta}{r}}\,dx_1, \quad H_2' = \frac{dr}{dx_1} = \sqrt{1 - \frac{2\alpha\beta}{r}},$$

and

$$\begin{aligned}(ds)^2 &= (dx_1)^2 + H_2^2(dx_2)^2 + H_3^2(dx_3)^2 + H_4^2(dx_4)^2 \\ &= \frac{(dr)^2}{1 - \frac{2\alpha\beta}{r}} + r^2(dx_2)^2 + r^2 \sin^2 x_2 (dx_3)^2 + \frac{1}{\beta^2}\left(1 - \frac{2\alpha\beta}{r}\right)(dx_4)^2 \dagger.\end{aligned}$$

With an obvious modification of the notation this is the classical result.

In the paper referred to at the beginning of this paper, what is done is to determine x_1 such a function of r that $H_2 = rH_1$.

We have $dx_1 = H_1 dr = H_2 \frac{dr}{r}$; whilst $\frac{dH_2}{dx_1} = \sqrt{1 - \frac{2\alpha\beta}{H_2}}$. So that

$$\frac{dH_2}{H_2\sqrt{1 - \frac{2\alpha\beta}{H_2}}} = \frac{dr}{r};$$

whence

$$H_2 - \alpha\beta + \sqrt{H_2^2 - 2\alpha\beta H_2} = Cr,$$

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* If we put $\phi'' = 0$, $\phi' =$ constant, and $\gamma = 0$.

† Another solution (corresponding to $\phi' =$ constant) is

$$(ds)^2 = \frac{-r(dr)^2}{2\alpha\beta} + r^2\left\{(dx_2)^2 + x_2^2(dx_3)^2\right\} - \frac{2\alpha}{\beta r}(dx_4)^2.$$

where C is a constant, or

$$2(H_2-\alpha\beta) = Cr+\frac{\alpha^2\beta^2}{Cr}.$$

Writing $\alpha\beta=m$, $C=2$, we obtain

$$H_2-m = r+\frac{m^2}{4r}, \quad \text{or} \quad H_2 = r\left(1+\frac{m}{2r}\right)^2;$$

whence

$$H_1 = \left(1+\frac{m}{2r}\right)^2,$$

$$H_4 = \frac{1}{\beta}\frac{dH_2}{dx_1} = \frac{1}{\beta}\frac{\partial H_2}{\partial r}\frac{dr}{dx} = \frac{1}{\beta}\left(1-\frac{m^2}{4r^2}\right)\frac{1}{H_1} = \frac{1}{\beta}\frac{1-\dfrac{m}{2r}}{1+\dfrac{m}{2r}};$$

and then

$$(ds)^2 = \left(1+\frac{m}{2r}\right)^4\left[(dr)^2+r^2\,dx_2{}^2+r^2\sin^2 x_2(dx_3)^2\right]$$

$$+\frac{1}{\beta^2}\left(\frac{1-\dfrac{m}{2r}}{1+\dfrac{m}{2r}}\right)^2(dx_4)^2,$$

which is essentially the result of the paper quoted.

It may be interesting, in conclusion, to say a few words about the case where $\phi'=0$, so that H_3 is a function of x_1 alone, as are all the other coefficients. This will be interesting in connexion with certain axial-symmetric solutions of $G_{rs}=0$ if the coordinate lines x_1 are interpreted as geodesics though not necessarily through a fixed point in the sub-space of three dimensions $x_4=\text{const.}$ G_{12} is now automatically zero for the same reason as are all the other components G_{rs}, $r\neq s$; (B) yields

$$\frac{H_2''}{H_2}+\frac{H_3''}{H_2}+\frac{H_4''}{H_4} = 0,$$

where primes denote as before differentiations with respect to the only variable occurring, x_1.

From (C) we have

$$H_2H_3H_4' = \text{constant} = c_4 \text{ (say)},$$

where the constant c_4 may be zero (taking care of the case $H_4'=0$ tacitly omitted on division across by H_4' before integration).

(D) gives on division by H_2H_2' and integration

$$\underline{H_2'H_3H_4 = \text{constant} = c_2,}$$

where as before c_2 may be zero.

(E) yields similarly

$$\underline{H_3'H_2H_4 = c_3.}$$

These equations may be written symmetrically

$$\frac{H_4'}{c_4H_4} = \frac{H_2'}{c_2H_2} = \frac{H_3'}{c_3H_3} = \frac{1}{H_2H_3H_4},$$

it being understood that if c_4, for example, is zero we omit this member of the equations and write instead

$$H_4' = 0 \quad \text{or} \quad H_4 = \text{constant}.$$

It is apparently advisable to write $l_2 \equiv \log H_2$ etc., and we have

$$\frac{l_4'}{c_4} = \frac{l_2'}{c_2} = \frac{l_3'}{c_3} = \frac{1}{H_2H_3H_4}$$

or

$$\frac{l_4''}{c_4} = \frac{l_2''}{c_2} = \frac{l_3''}{c_3} = -\frac{1}{H_2H_3H_4}(l_2' + l_3' + l_4').$$

Suppose, for example, $c_2 \neq 0$ and eliminate l_3 and l_4 and obtain

$$l_2'' = -l_2'\left(l_2' + \frac{c_3}{c_2}l_2' + \frac{c_4}{c_2}l_2'\right);$$

whence

$$\frac{1}{l_2'} = \left(\frac{c_2 + c_3 + c_4}{c_2}\right)(x_1 + \text{const.}).$$

Choosing the origin of measurement of x_1 so that this additive constant is zero, we obtain

$$l_2' = \frac{c_2}{c_2 + c_3 + c_4} \cdot \frac{1}{x_1}.$$

$$\therefore \quad \log H_2 = \frac{c_2}{c_2 + c_3 + c_4} \log x_1 + \text{const.}$$

$$\text{or} \quad H_2 = C_2 x_1^{\frac{c_2}{c_2+c_3+c_4}}; \quad H_3 = C_3 x_1^{\frac{c_3}{c_2+c_3+c_4}};$$

$$H_4 = C_4 x_1^{\frac{c_4}{c_2+c_3+c_4}}.$$

(There is an exceptional case, $c_2 + c_3 + c_4 = 0$. Here

$$l_2'' = 0, \qquad l_2' = \text{const.} = c_2k \text{ (say)}.$$

Then

$$l_2 = c_2 k x_1 + \alpha\,; \quad l_3 = c_3 k x_1 + \beta\,; \quad l_4 = c_4 k x_1 + \gamma,$$

where α, β, γ are constants.) The constants C_2, C_3, C_4 or α, β, γ respectively are not independent. We have

$$C_2 C_3 C_4 = c_2 + c_3 + c_4 \quad \text{or} \quad \alpha + \beta + \gamma + \log k = 0.$$

There remains the equation

$$\frac{H_2''}{H_2} + \frac{H_3''}{H_3} + \frac{H_4''}{H_4} = 0,$$

or

$$l_2'' + l_2'^2 + l_3'' + l_3'^2 + l_4'' + l_4'^2 = 0.$$

Again eliminating l_3 and l_4,

$$l_2''\left\{1 + \frac{c_3}{c_2} + \frac{c_4}{c_2}\right\} + l_2'^2\left\{1 + \frac{c_3^2}{c_2^2} + \frac{c_4^2}{c_2^2}\right\} = 0.$$

This shows (a) that if $c_2 + c_3 + c_4 = 0$ then $l_2' = 0$ (giving the trivial Euclidean case) unless $c_2^2 + c_3^2 + c_4^2 = 0$, in which case all the equations are satisfied.

Hence we have the solution

$$\begin{aligned}(ds)^2 &= (dx_1)^2 + e^{2c_2x_1}(dx_2)^2 + e^{2c_3x_1}(dx_3)^2 + e^{2c_4x_1}(dx_4)^2 \\ &= \frac{1}{r^2}(dr)^2 + r^{2c_2}(dx_2)^2 + r^{2c_3}(dx_3)^2 + r^{2c_4}(dx_4)^2,\end{aligned}$$

where $r = e^{x_1}$, and c_2, c_3, c_4 are three constants satisfying the two equations

$$c_2 + c_3 + c_4 = 0\,; \quad c_2^2 + c_3^2 + c_4^2 = 0.$$

(We have suitably modified the units in which x_1, x_2, x_3, x_4 are measured.)

(b) If $c_2 + c_3 + c_4 \neq 0$ we have

$$-\frac{l''}{l_2'^2} = \frac{c_2^2 + c_3^2 + c_4^2}{c_2(c_2 + c_3 + c_4)} = \frac{c_2 + c_3 + c_4}{c_2}$$

from a previous equation ; yielding

$$c_2c_3 + c_3c_4 + c_4c_2 = 0.$$

(This relation is equivalent to $\frac{H_2}{H_2'} + \frac{H_3}{H_3'} + \frac{H_4}{H_4'} = 0$ if none of the c's $= 0$.) If, then, we choose three constants c_2, c_3, c_4

satisfying this relation

$$c_2c_3+c_3c_4+c_4c_2 = 0$$

and whose sum is unity * we have that

$$(ds)^2 = (dx_1)^2+x_1{}^{2c_2}(dx_2)^2+x_1{}^{2c_3}(dx_3)^2+x_1{}^{2c_4}(dx_4)^2$$

will satisfy Einstein's equations $G_{rs}=0$. However, a detailed examination of all possibilities is out of place here. It will suffice if we have shown that the Einstein differential equations are of a regular character and are exactly integrable in a large variety of cases.

III. *On the Separation of the Isotopes of Mercury.*

By J. N. BRØNSTED *and* G. HEVESY †.

1. *Introduction.*

THE hypothesis, based on various considerations, that isotopy, hitherto found only within the domain of the radioactive elements, may be finally proved to be a general property of matter, has been established by Aston's ‡ brilliant experiments. The question of the separation of isotopes, already much discussed in radio-chemistry, has become thereby a problem of still more general importance. We have already elsewhere § given brief accounts of the results of some experiments made in this laboratory on the separation of isotopes. The present paper contains a closer description of the principles and the methods used, together with the results of further experiments.

2. *On some methods of separating of Isotopes.*

On account of the chemical properties of the atom being materially independent of its mass, only a few methods of separation come into consideration—chiefly, those which make use of the difference in the molecular velocities (atomic

* The units of measurement of x_2, x_3, x_4 can be so chosen that C_2, C_3, C_4 in the equations $H_2=C_2\ x_1{}^{\frac{c_2}{c_2+c_3+c_4}}$ etc. above all equal unity and this necessitates $c_2+c_3+c_4=1$ since $C_2C_3C_4=c_2+c_3+c_4$.

† Communicated by the Authors.

‡ Aston, Phil. Mag. xxxviii. p. 707 (1919); xxxix. pp. 449, 611 (1920); xl. p. 628 (1920).

§ 'Nature,' cvi. p. 144 (1920); cvii. p. 619 (1921).

velocities) appearing as a consequence of the mass difference of the isotopes. That is for instance the case with an incomplete reaction between a solid or liquid and a highly diluted gaseous phase *, and thus also with a partial evaporation or condensation which belong to the most simple heterogeneous reactions. If a liquid is in equilibrium with its vapour, then in unit time a certain number of vapour molecules will hit its surface and adhere; in order to keep up the state of equilibrium, it is necessary that in unit time the same number of molecules pass from the liquid into the vaporous phase. The velocity of exchange of molecules between the two phases depends upon the density of the vapour and the velocity of the vapour molecules; the quicker the latter, the more vapour molecules will reach the surface in the time-unit and the livelier will be the exchange of molecules between the two phases.

We will now consider a liquid containing two isotopes in equal amounts. As in this case the vapour-pressure of the two isotopes is equal, the vapour phase will have the same composition as the liquid. Notwithstanding this equality in the composition of the two phases, a livelier exchange will take place between the lighter than between the heavier atoms in the two phases. The former have, namely, in accordance with their smaller mass (m_1), a velocity (v_1) $\sqrt{\frac{m_2}{m_1}}$ times as great as the latter—the mass and velocity of which we will denote by m_2, respectively v_2—and so in the time-unit $\sqrt{\frac{m_2}{m_1}}$ times as many molecules of the lighter as of the heavier isotope will be transferred from the liquid in the vaporous stage, and *vice versa*. As long as an

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* A concrete example best explains these conditions. If chlorine gas is passed through a silver tube and only a small fraction of the molecules is assumed to react with the metal, then on account of the greater molecular velocity of the lighter isotope the molecules of this will have a greater probability of hitting the wall of the silver tube than the molecules of the heavier one have. More of the lighter chlorine will therefore be bound as silver chloride than of the heavier, and—as a simple estimate shows—the ratio will under the most favourable conditions equal $\sqrt{\frac{37}{35}}$ times the ratio of the isotopes in the gaseous phase.

By this estimate, however, the possibility of the result of an impact being influenced by the velocity of the molecules is neglected, as well as the fact that besides $(Cl^{35})_2$ and $(Cl^{37})_2$, also $(Cl^{35}Cl^{37})$ molecules are present in the gaseous phase.

evaporation under usual conditions is considered, we are not in the position to utilize the quicker movements of the lighter molecules for the purpose of separating isotopes, because the quicker evaporation in the case of the lighter molecules is just compensated by a quicker re-condensation. We can, however, prevent this compensation by suppressing one of the two compensating processes; and on the grounds of this principle we are able to reach a simple method for a partial separation of the isotopes. This is most easily accomplished by allowing the liquid to evaporate in a vacuum and placing a highly-cooled glass plate over its surface. Now when the vapour-pressure of the liquid is sufficiently slight, each molecule which leaves the liquid will reach the cooled wall before it has had an opportunity of meeting other molecules and being thrown back into the liquid. Having reached the cooled wall, it will be held by it, transferred into the solid state, and hindered in re-evaporation. It follows from the above that in the "ideal distillate" obtained in this way there will be $\sqrt{\frac{m_2}{m_1}}$ times as much of the lighter isotope as in the initial substance, and through repeated "ideal distillations" of the fractions thus obtained it is possible to carry the partial separation further.

The applicability of the evaporation method depends on two conditions: (*a*) a not too great vapour-pressure of the liquid and a very good vacuum, in order to avoid collision of the evaporating molecules with each other or with other molecules contingently present which would cause reflexion and return to the liquid phase; (*b*) equal composition of the surface and interior of the liquid phase. If the velocity of the exchange of atoms between the liquid surface and the liquid body be insufficient, then the heavier isotope will be concentrated in the surface layer and soon render all further separation impossible.

As we shall see later on (§ 3), these conditions in most cases do not in any way render the evaporation method impracticable as long as the substance to be separated is in a liquid state; while, on the other hand, the requirement of the condition (*b*) practically excludes the use of this method in the case of a solid substance.

The second separation method used by us is the effusion process. If a molecular flow * of an isotopic vapour takes

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* Knudsen, *Ann. der Physik*, (4) xxviii. p. 999 (1909). R. W. Wood, Phil. Mag. xxx. p. 300 (1915).

place through a narrow opening, then the lighter isotope (molecular weight m_1), which in consequence of its greater molecular velocity hits the opening comparatively more often than the heavier, will have a greater probability for penetrating the opening than the latter (molecular weight $=m_2$). As the molecules which pass through the opening are soon condensed on the other side at low temperature, the probability that they are able to go the reverse way is very slight. If in the initial substance the two isotopes were present in the proportion 1 : 1, and only a small fraction pass through the narrow opening, we must expect the two isotopes on the other side of the opening to be present in the proportion $\sqrt{\frac{m_2}{m_1}}$.

As in the case of the evaporation method, the method here mentioned therefore admits under the most favourable conditions a separation proportional to the square root of the ratio of the two molecular weights. Although not favourable from a practical point of view on account of the slowness of the effusion process, this method is of theoretical importance, and was therefore also used by us in our experiments with mercury.

3. *Separation of the Mercury Isotopes based on the difference in their evaporation velocity.*

A number of reasons have induced us to begin the series of mixed elements, to be separated into pure elements, with mercury. The vapour-pressure of this substance can be varied in the particularly handy temperature-range 0°–100° within wide limits, embracing a practically negligible pressure as well as the already considerable one of about 0·3 mm.; besides this, the free mean path and other magnitudes important for the kinetic theory of gases are well known in the case of mercury. There is hardly another substance which can be produced in a pure state with so little labour, and no substance of which the density can be determined so easily and exactly. A density determination is certainly the most easily approachable and the most exact manner for determining a partial or complete separation of isotopes. The volume of the isotopic atoms is, as is well known, equal[*]; so that by comparing the density of the "normal" and "separated" mercury, a separation can be easily detected and its degree measured.

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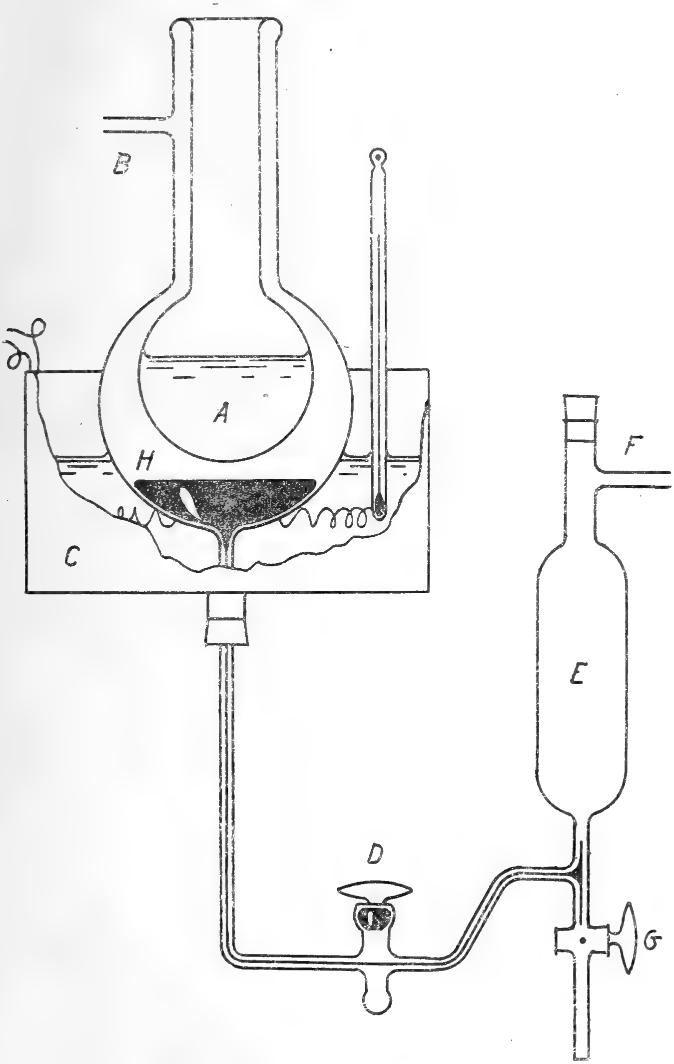
[*] Compare the agreement found by Th. W. Richards and Ch. Wadsworth (Journ. Amer. Chem. Soc. xxxviii. p. 221, 1916), F. Soddy ('Nature,' cvii. p. 41, 1921), and especially the conclusion following from Bohr's spectral theory.

(a) *The experimental method.*

In separating the mercury isotopes the following arrangement was used:—In the space H between the outer and inner flask of the Dewar vessel (fig. 1) about 300 c. cm. mercury were placed, H thoroughly evacuated by means of a Vollmer pump which was connected at B, and the inner

Fig. 1.



vessel A filled with liquid air. The distance between the mercury and the cooled glass surface was 1–2 c. cm. As evaporation proceeds rather slowly at room-temperature, the mercury was heated to about 40°–60° by means of the surrounding oil-bath C. After a suitable portion of the mercury was evaporated, we removed the remaining "heavier" part by evacuating the receiver E and opening the cock D, whereby the mercury by its own weight flowed into the receiver and could be taken out through the cock G. The liquid air was now allowed to evaporate, whereafter the solid mercury melted, dropped into the bottom of H, and was removed from there in just the same way as the "heavier" mercury. The operation was now repeated with another sample of ordinary mercury, and so on until a total of about 2700 c. cm. was separated in a distilled (D_1) and a residual fraction (R_1).

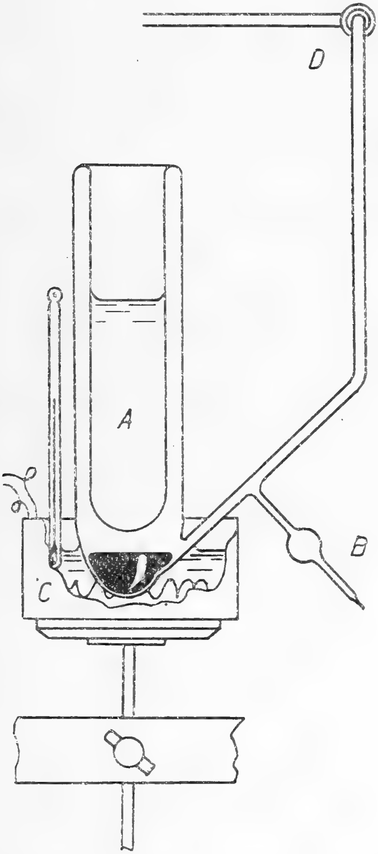
In order to obtain heavier mercury, R_1 and the following R-fractions were subjected to further similar separations. When lighter mercury was desired, D_1 and the following D-fractions were treated in the same way.

For smaller quantities of mercury, as available in the later part of our work, we used two apparatus, as shown in fig. 2, with a capacity of 40 and 8 c. cm. and working as follows:—

After having finished the evaporation, the residual mercury is removed by turning the ground-joint at D and thus the whole apparatus about 50°, which permits the mercury to flow into the bulb B. Now the vacuum is destroyed, the point of the capillary tube broken off, and the outflowing mercury caught. The solid mercury, which after evaporation drips off and gathers in the lower space, is then removed in a similar manner.

By using the arrangement shown in fig. 1 at 45°, about 6 c. cm. mercury evaporated per hour, corresponding to an evaporation of 0·35 c. cm. per cm.^{2} At this temperature the vapour-pressure of the mercury amounts to about 0·01 mm., and the mean free path, in so far as the vapour can be considered as stationary, about 10 mm. Ideal separating conditions were thus nearly fulfilled at this temperature. Yet the evaporating process can be carried out more swiftly without thereby reducing the degree of the separation. For instance, by working at 120° and using the apparatus represented in fig. 2, the large amount of 1·5 c.cm. per hour and per square cm. evaporated; yet the degree of separation achieved was found to be only slightly smaller than the one obtained under "ideal" conditions. At 120° the vapour-pressure of mercury already attains the value of 0·7 mm., and the mean free path is accordingly only 0·15 mm.—only quite a small fraction of the distance between the mercury and the cold glass surface. That the separation succeeded in spite of this is explained by the fact that the current of the mercury vapour from the warm to the cold surface is onesidedly directed, and that the presence of the steep gradient hinders the retreat of the evaporated molecules into the liquid. Under these conditions "the mean free path" surmounts many times the mean free path of the mercury molecules experienced under normal conditions.

Fig. 2.



From the fact that even by rather rapid evaporation a partial separation of the mercury isotopes can be achieved, we are justified in concluding that the exchange of the mercury molecules between the surface-layer and the interior of the liquid is also rapid; for it is clear that a slow exchange of molecules would lead to an accumulation of the heavier isotope in the surface-layer, thus frustrating the separation. In so far as the exchange is only accomplished by diffusion, the time required can be approximately calculated. We can, namely, determine approximately the velocity with which mercury diffuses in mercury (self-diffusion) from the known diffusion-rate of lead in mercury*. The latter† at the temperature of 100° equals about $3 \cdot 10^{-5}$ cm.^{2}/sec.$^{-1}$, and as the mean displacement square of the molecule per sec. depends on the diffusion-constant (D) as in the equation

$$\tau^2 = 2D,$$

then the mean displacement (τ) of the mercury molecules in the liquid mercury is about $5 \cdot 10^{-3}$ cm./sec.$^{-1}$. It follows from this calculation that if not more than $5 \cdot 10^{-3}$ c. cm. per cm.^{2} surface evaporates during the time-unit, no disturbing accumulation of the heavier isotope in the surface-layer takes place.

(b) *The experimental results.*

As initial material, 2700 c. cm. of the purest mercury was used. This was submitted, in portions of about 300 c. cm., to an "ideal distillation" in the large apparatus (fig. 1), and the process continued until about a fourth of the mercury was distilled over. A total of 2062 c. cm. residual and 642 c. cm. distilled substance, which we will denote by R_1 and D_1, was acquired.

In order to obtain heavy mercury, R_1 was submitted to a similar treatment as the initial material, and 1602 c. cm. residual (R_2) and 460 c. cm. distillate (R_1D_1) acquired. By proceeding in the same manner, continuously decreasing remainder volumes (R_3, R_4, . . .) of continuously increasing density were obtained. Beginning from R_{10}, the volume of the mercury became too small to be treated in the large apparatus; so first the middle-sized, and from R_{14} onwards the small apparatus was used.

The progression of the experiment in the case of the residual mercury is shown in Table I., which contains the densities found with the density of ordinary mercury as unity.

As seen from the table, the density of the R-fractions increases gradually as the residual volume decreases, and ultimately in the case of the heaviest mercury becomes $\frac{1}{4}$ ‰ larger than the density of the normal substance.

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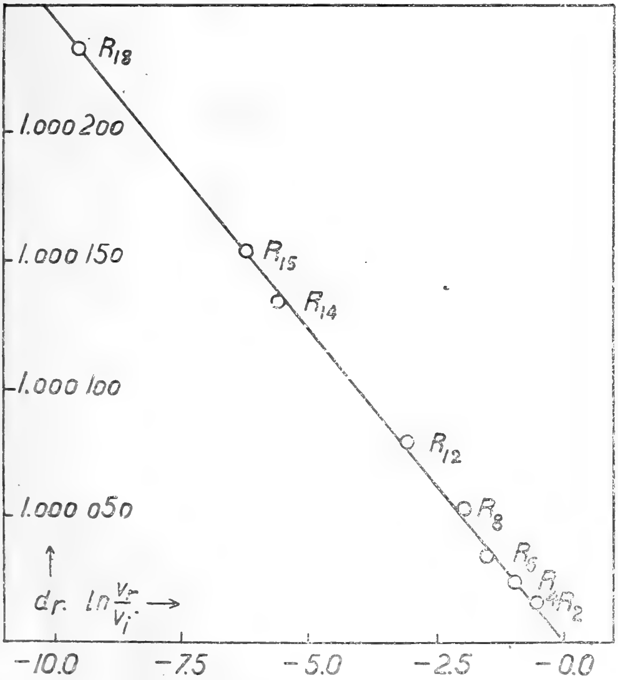
* Compare Gröh & Hevesy, *Ann d. Phys.* lxiii. p. 92 (1920).

† M. Knudsen, *Ann. d. Physik*, (4) xxix. p. 179 (1909).

TABLE I.

Fraction.	Volume.	Density.	Fraction.	Volume.	Density.
D_1	642	0·999977	R_1	2062	—
R_1D_1	461	0·999989	R_2	1602	1·000016
R_2D_1	320	—	R_3	1283	—
R_3D_1	243	—	R_4	1030	1·000024
R_4D_1	235	—	R_5	791	—
R_5D_1	202	—	R_6	585	1·000034
R_6D_1	94	—	R_7	489	—
R_7D_1	115	—	R_8	382	1·000053
R_8D_1	105	—	R_9	268	—
R_9D_1	82	—	R_{10}	185	—
$R_{10}D_1$	35	—	R_{11}	150	—
$R_{11}D_1$	22	—	R_{12}	128	1·000079
$R_{12}D_1$	87	1·000060	R_{13}	42	—
$R_{13}D_1$	31·5	1·000090	R_{14}	10·3	1·000134
$R_{14}D_1$	4·8	—	R_{15}	5·5	1·000153
$R_{15}D_1$	4·4	—	R_{16}	1·1	—
$R_{16}D_1$	0·5	—	R_{17}	0·5	—
$R_{17}D_1$	0·3	—	R_{18}	0·2	1·00023

Fig. 3.



These results are also shown in fig. 3, where the density is plotted as ordinate and the abscissa represents the natural logarithm of the ratio of the remainder and the initial volume. The significance of the rectilinear course as shown in the figure is explained by equation (7) in § 5.

In order to obtain light mercury, D_1 has been submitted to a further distillation, and thus separated into a distillate D_2 and a residue D_1R_1 ; D_2 has been treated in the same way, and so on. The results of the first five experiments of this series appear in Table II.

TABLE II.

Fraction.	Volume.	Density.	Fraction.	Volume.	Density.
			D_1	642	0·999977
D_1R_1	472	0·999979	D_2	154	0·999953
D_2R_1	101	0·999961	D_3	50	0·999933
D_3R_1	35·5	0·999941	D_4	13·5	0·999911
D_4R_1	10	0·999914	D_5	3·3	0·999881

As was to be expected, the D-fractions exhibit continuously decreasing densities. From D_5 onwards the systematic treatment described above could no longer be applied favourably on account of the small amount of the material left. It was therefore found profitable to make residues of distillates of high order the material of departure for further distillations, and to unite the various portion of similar density obtained in this way. It was thus possible to increase essentially the otherwise quickly decreasing quantities of the higher-order fractions. The results are given in Table III.

TABLE III.

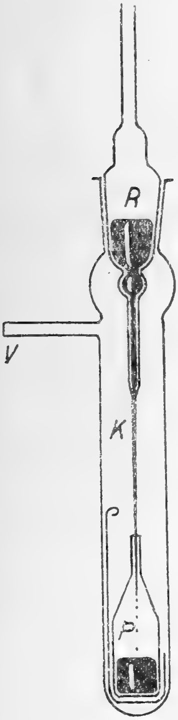
Fraction.	Volume.	Density.
D_6	7·0	0·999874
D_7	3·9	—
D_8	2·3	0·999824
D_9	0·9	0·999779
D_{10}	0·7	—
D_{11}	0·55	—
D_{12}	0·5	—
D_{13}	0·4	—
D_{14}	0·2	0·99974

The densities are seen to be steadily decreasing. The lightest mercury possesses a density deviating from that of the ordinary mercury by about $\frac{1}{4}$ $^0/_{00}$—the same deviation as shown by the heaviest mercury in opposite direction. The density difference between the heaviest and lightest mercury therefore amounts to nearly $\frac{1}{2}$ $^0/_{00}$.

4. *The density determination.*

As has already been mentioned, in determining the partial separation of the mercury isotopes, density measurements of the fractions gained through the described separation method were used. The atomic volume of the isotopes being equal, the change in density offers a simple measure of the change in the element weight * as achieved by separation. Fig. 4 shows the arrangement used for the density determinations.

Fig. 4.



The mercury is brought into the reservoir R, which ends below in a capillary tube K sufficiently narrow to prevent the mercury from running out when left alone. The capillary is inserted into the 0·3 mm. narrow neck of the little bottle P. When tube V is connected with the Gaede pump, the overpressure resulting drives the mercury through the capillary, and the pyknometer is slowly filled with mercury. R is now removed, the pyknometer placed in a thermostat for about an hour and a half, and after removing the drop of mercury, expelled by the heating, weighed. We employed two pyknometers, of which the volumes amounted to about 5 and 1·3 cm.^{3} respectively. By using the first the density could be determined with an accuracy of $2:10^6$, with the second the accuracy was correspondingly less. For determining quite small volumes (about 0·2 cm.^{3}) of the heaviest and lightest fractions, a thick-walled glass tube of 0·1 mm. inner diameter, with both ends drawn out very fine, was used as a pyknometer. The mercury was sucked into the pyknometer when held in vertical position, and as it could not run out by itself into the vacuum through the very fine upper opening, the tube could be placed in reversed position in the thermostat. On account of the slight volume of this capillary pykometer, such exact measurements cannot be made with it as with the one of larger capacity. The capillary pyknometer, however, was only used in cases in which the change in density was already very considerable.

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* The term *element weight* is used for the mean atomic weight of the mix-element: see Harkins, J. Am. Ch. Soc. xliii. p. 1038 (1921).

The mercury used in the density determination was present in the purest state. In each fraction examined we made sure that any further vacuum-distillation made in the usual way had no influence on the density of mercury within the limit of our errors of measurement.

5. *Calculation of the separation.*

In the case of a mix-element composed of two isotopes, to be separated into its components by means of the evaporation method described, the change which the element weight suffers through a single evaporation can be calculated in the following way. If N_1 and N_2 are the number of molecules originally present, n_1 and n_2 are those of the evaporated molecules of the first resp. second isotope, M_1 and M_2 the corresponding molecular weights (atomic weights); then, granted the above-mentioned ideal conditions (p. 33), the differential equation fundamental to our calculation,

$$\frac{dn_1}{dn_2} = \frac{N_1 - n_1}{N_2 - n_2} \sqrt{\frac{M_2}{M_1}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

follows; from which, by integration, we obtain

$$\ln \frac{N_1 - n_1}{N_1} = \sqrt{\frac{M_2}{M_1}} \ln \frac{N_2 - n_2}{N_2}.$$

In the special case, which we will deal with first, where the initial ratio of the two isotopes is equal to unity, we can put

$$N_1 = N_2 = 1,$$

and further

$$M_1 = M_i(1 - \Delta), \quad M_2 = M_i(1 + \Delta),$$

where M_i indicates the element weight of the mix-element in its original state. We then obtain

$$\frac{\ln(1 - n_1)}{\ln(1 - n_2)} = \sqrt{\frac{1 + \Delta}{1 - \Delta}},$$

or with great approximation

$$\frac{\ln(1 - n_1)}{\ln(1 - n_2)} = 1 + \Delta. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Taking into consideration that the element weight of the fraction remaining after distillation is expressed by

$$M_r = \frac{(1 - n_1)M_1 + (1 - n_2)M_2}{2 - (n_1 + n_1)}, \quad . \quad . \quad . \quad (3)$$

and the ratio between the initial volume and that remaining after distillation by

$$\frac{v_i}{v_r} = \frac{2}{2-(n_1+n_2)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

we obtain

$$\frac{\mathrm{M}_r}{\mathrm{M}_i} = 1+(n_1-n_2)\frac{\Delta}{2}\frac{v_i}{v_r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

or

$$\left.\begin{aligned} 1-n_1 &= \frac{v_r}{v_i}\left(1+\frac{1-\dfrac{\mathrm{M}_r}{\mathrm{M}^i}}{\Delta}\right), \\ 1-n_2 &= \frac{v_r}{v_i}\left(1-\frac{1-\dfrac{\mathrm{M}_r}{\mathrm{M}_i}}{\Delta}\right). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Introducing the two latter equations into (2), and denoting the ratio of the element weights $\frac{\mathrm{M}_r}{\mathrm{M}_i}$, which is equal to the corresponding densities, by d_r—the meaning of this magnitude being nothing but the density of the remaining part expressed in terms of that of the standard substance—we obtain

$$\frac{\ln\dfrac{v_r}{v_i}+\dfrac{1-d_r}{\Delta}}{\ln\dfrac{v_r}{v_t}-\dfrac{1-d_r}{\Delta}} = 1+\Delta,$$

or, transformed,

$$1-d_r = \frac{\Delta^2}{2+\Delta}\ln\frac{v_r}{v_i}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

By means of this equation from the known ratio $\frac{v_r}{v_i}$ and the relative density of the residue d_r, Δ and thus the molecular weight (atomic weight) of both the pure elements can be calculated. The validity of the above equation can be tested by proving that it can be satisfied for all corresponding d_r and $\frac{v_i}{v_r}$ values by a single Δ value. This is possible when calculating the density of our mercury residue (d_r) from equation (7), on the assumption that Δ has the constant value 0·0070.

The results of this calculation, as well as the densities experimentally determined, are shown in Table IV.

TABLE IV.

Fraction.	Density found.	Density calc.	Fraction.	Density found.	Density calc.
R_2	1·000016	1·000013	D_1	0·999977	0·999979
R_4	1·000024	1·000024	D_2	0·999953	0·999956
R_6	1·000034	1·000038	D_3	0·999933	0·999935
R_8	1·000053	1·000048	D_4	0·999911	0·999913
R_{12}	1·000079	1·000075	D_5	0·999881	0·999890
R_{14}	1·000134	1·000137			
R_{15}	1·000153	1·000152			
R_{18}	1·00023	1·000234			

As the figures found and calculated agree very well, we may conclude, as will be more elaborately explained later,that the evaporation of the mercury in our experiments took place according to the theoretical supposition (reversed proportion of the evaporation velocity to the square root of the atomic weight). Further, that the separating process of the mercury proceeds like that of a mixture consisting of equal parts of two pure elements with the atomic weights:

$$M_1 = M_i(1+\Delta) = 200{\cdot}6\,.\,1{\cdot}0070 = 202{\cdot}0,$$
$$M_2 = M_i(1-\Delta) = 200{\cdot}6\,.\,0{\cdot}9930 = 199{\cdot}2.$$

The results are also represented in fig. 4, exhibiting clearly the fulfilment of the requirement of a rectilinear interdependancy between the density and $\ln\frac{v_r}{v_i}$ as follows from equation (7).

As already mentioned, the above calculation presupposes that the two constituting pure elements are present in the mix-element in equal atomic proportions. If this supposition is omitted, there is an infinite number of M_1 and M_2 values which are compatible with the value of M_i, and corresponding to each of these cases a separate shape of the separation curve (representing the interdependance between the density d_r and the volume of the residue) is furnished. For evaluating this fact in determining the atomic weights, it is necessary, however, to consider a longer portion of the curve than the one corresponding to our experimental results. If we only consider the result of the first separating operations, practically coincident curves may be found also where the number of atoms and therefore also the atomic weights of the two pure elements in the mixed element vary. In order to further illuminate this point, we proceed from the expressions (8) and (9) representing the atomic weight of the unchanged mix-element, and that of the first distillate, in so far as the distilled amount is a small one :

$$M_i = \frac{N_1 M_1 + N_2 M_2}{N_1 + N_2}, \quad \ldots \ldots \quad (8)$$

$$M_d = \frac{N_1\sqrt{M_1} + N_2\sqrt{M_2}}{\dfrac{N_1}{\sqrt{M_1}} + \dfrac{N_2}{\sqrt{M_2}}}. \quad \ldots \ldots \quad (9)$$

When we write $\frac{N_1}{N_2} = \alpha$ and $\frac{M_1}{M_2} = \beta^2$, we find

$$\frac{M_i}{M_d} = \frac{(\alpha+\beta)(\alpha\beta^2+1)}{\beta(\alpha+1)(\alpha\beta+1)}, \quad \ldots \ldots \quad (10)$$

which, when the atomic weights M_1 and M_2 are not too unlike, is practically identical with the following :

$$\frac{M_i}{M_d} - 1 = \frac{1}{d_d} - 1 = \frac{2\alpha}{(1+\alpha)^2}(\beta-1)^2, \quad \ldots \quad (11)$$

where d_d denotes the density of the first distillate. The value of d_d can either be directly determined from the result of a single distillation, or with greater accuracy from the Δ value with the aid of the equation :

$$d_d = \sqrt{1-\Delta^2}. \quad \ldots \ldots \quad (12)$$

This expression inserted in equation (11) gives finally

$$\frac{2\alpha}{(1+\alpha)^2} \cdot (\beta-1)^2 = \frac{\Delta^2}{2-\Delta^2}, \quad \ldots \ldots \quad (13)$$

or for small values of Δ :

$$\frac{2\alpha}{(1+\alpha)^2}(\beta-1)^2 = \frac{\Delta^2}{2}. \quad \ldots \ldots \quad (14)$$

If Δ is given, then in equation (14) to each value of α there is only one single β value—that is, when in addition to the experimentally determined Δ the proportion in which the pure elements are present in the mix-element is known, the atomic weight of the pure elements can be determined *.

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* The equation (14) lends to the magnitude Δ (defined initially as relating to the case where the mix-element contains the two pure elements in equal amounts) a more general significance when interpreting separation results.

In the case of mercury, where, as already mentioned, $\Delta=0{\cdot}0070$, the following values of β, M_1 and M_2 correspond to the values of α given in the first column of the table.

TABLE V.

α.	β.	M_2.	M_1.	M_2-M_1.
1	1·00702	202·0	199·2	2·8
4	1·00877	201·3	197·8	3·5
9	1·01171	201·1	196·7	4·7

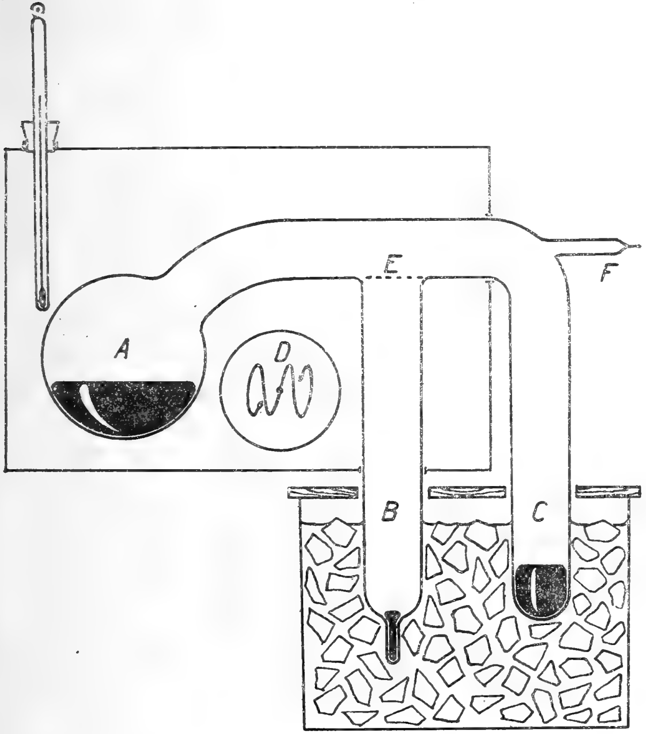
Consequently we are able to interpret our experimental results by assuming the ordinary mercury as made up of the pure elements 202·0 and 199·2 present in equal amounts or by the elements 201·3 and 197·8, where the former is four times as strongly represented as the latter, and so on. Our results agree with those of Aston's, found by means of his mass-spectrograph, in the fact that Aston found a strong line corresponding to the atomic weight 202 and an undissolved band the centre of which corresponds to about 199. A very slight quantity of an isotope with the atomic weight of 204, the presence of which follows from Aston's experiments, cannot be found by our method if the separation is not to be pursued very considerably farther.

For the numeric calculation stated above, we used the results of density measurements made on residual fractions. The calculation can also be carried out by using density data of the distilled fractions, or reversely the course of the distillation process can be predicted by means of the values furnished by measurements on residual fractions. Whilst the production of the heavy fraction consisted in a steady evaporation of the initial volume 2700 c. cm. until only 0·2 c. cm. was left, we were for practical reasons—dimensions of our apparatus and working economy—obliged to mix distillates of different quality when endeavouring to produce the most valuable light fraction. The calculation of the separation proceedings on the basis of the density of the lighter fractions is therefore rendered somewhat complicated. In spite of this, the calculated d_d values as shown in Table IV. agree fairly well with the ones determined, though the conformity is not as good as in the case of the d values of the residual fractions.

Separation of the Mercury Isotopes using the Effusion Method.

Fig. 5 represents an apparatus used for the separation of the isotopes based on the method described on p. 34. The main quantity of the mercury vapour passes from the heated bulb A into tube C cooled with ice, and only a fraction of the vapour has the opportunity of entering the equally cooled tube B by passing one of the numerous holes in a platinum foil inserted in the glass tube at E. The diameter of the platinum foil, as well as that of the glass tube, is 2 cm. and it has 1000 holes of 0·15 mm. diameter each. The whole apparatus was thoroughly exhausted.

Fig. 5.



As found by Knudsen *, the rule of the molecular flow through a narrow opening is only strictly valid when the

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* *Ann. d. Physik,* (4) xxviii. p. 999 (1909) ; xxix. p. 179 (1909).

mean free path of the molecules is more than ten times as great as the diameter of the opening. Knudsen, however, by using a 2·4 mm. wide opening and working at 59°·8, noted a deviation of only about 8 per cent. from what was calculated from the rule of the molecular flow, and it was to be expected that also by using essentially larger openings or a smaller mean free path the partial separation of mercury would be successful.

By heating the bulb A to 105°, corresponding to a mean free path of the mercury molecules of about 0·3 mm. at E, the product condensed in B showed the density 0·999987.

In this connexion we might mention that diffusion methods have been repeatedly employed in order to attain separation of the isotopes. Aston [*] was the first to use this method and got, in the case of neon, considerable changes in density. By means of a similar method, Stern and Volmer [†] have tried to separate the elements hydrogen and oxygen, yet without result, in accordance with their nature as pure elements. A trial to separate the isotopes of uranium through diffusion in aqueous solution was equally unsuccessful [‡].

Summary.

1. A partial separation of the isotopes of mercury based on the two methods following was successful.

(*a*) Evaporation method ("ideal distillation") based on the difference in the evaporation *velocities* of isotopes. The distillate was found richer, the remainder poorer in the lighter isotope, than the initial substance.

(*b*) Effusion method. A fraction of the mercury vapour penetrates through narrow openings into the condensation space, where the lighter isotope is found in a relatively larger amount than in ordinary mercury.

2. The results of the experiments agree with the theory, according to which the evaporation—as well as the effusion velocity of the isotopes—is inversely proportional to the square root of their molecular weights; they are further in conformity with Aston's results obtained by means of his mass spectrograph.

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[*] Brit. Assoc. Report, 1915; Phil. Mag. xxxix. p. 450 (1920). Compare also the following attempts:—D. Harkins, 'Nature,' cv. p. 230 (1920); E. Kohlweiler, *Zeitschr. f. Phys. Chem.* xcv. p. 95 (1920); and H. Grimm (K. Fajans, *Radioaktivität*, 3 Aufl., footnote p. 112).

[†] *Ann. d. Physik*, lix. p. 225 (1919).

[‡] Hevesy & Putnoky, *Phys. Zeitschr*. xiv. p. 63 (1913).

3. The partial separation achieved was proved by density measurements. The density difference found between the heaviest and lightest mercury amounts to 0·49 $^{0}/_{00}$, corresponding to a difference of 0·1 unit in the element weight of mercury.

In carrying out the experiments described here we are indebted to Mr. V. Thal-Jantzen for his valuable assistance.

Physico-Chemical Laboratory of the
Polytechnic Institute of Copenhagen.

IV. *On the Lags of Thermometers. By* A. R. McLeod, *M.A., Fellow of Gonville and Caius College, Cambridge* *.

In a former paper † expressions have been given for the steady lags in the mean temperatures of thermometers with spherical and cylindrical bulbs, when the external temperature increased at a constant rate and the initial temperature was zero everywhere. Under the same conditions, Dr. T. J. I'A. Bromwich ‡ has since given formulæ for the mean lags at all times until the steady value is reached. The present paper deals among other things with the lags for such thermometers, when the initial and surface conditions are somewhat different. The conditions were suggested to the author by Mr. E. Gold, and are based on experience in taking air temperatures by aeroplane in France.

The new conditions are obtained by warming up the thermometer initially to a fixed temperature, the external temperature being thereby initially unchanged, and by having a discontinuous surface condition, the temperature of the air (or other medium) changing linearly with time until a certain time t_1, and then changing linearly at a new rate.

Numerical values for mercury and alcohol agree with those given in the former paper. Using the same thermometer stem with each bulb, the alcohol cylinder is better than the mercury cylinder and both are decidedly superior to spheres. Owing to the fact that much finer capillary tubes may be used with mercury than with alcohol, the possibility exists of constructing mercury thermometers with much less

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* Communicated by the Author.

† Phil. Mag. xxxvii. Jan. 1919, p. 134.

‡ Phil. Mag. April 1919, p. 407.

lag than alcohol thermometers which have the same accuracy of reading.

A general expression is given for the steady lag of a bimetallic thermometer, used in air. The lags of some bimetallic recording thermometers considered are of the same order as those of the cylinders considered, but the comparison is not based on an equality of temperature scale. The lag of the Dines "ballon sonde" thermometer is very small.

Experiment shows that the mean surface conductivity for a bimetallic thermometer in the form of a flat spiral which is wound in a cylindrical tube, may be increased 34 per cent. by turning the thermometer from the "end on" position to the "broadside on" position in a wind of 5–10 m.p.h.

Radiation, convection, and the effects of the glass wall, in the case of liquid-in-glass thermometers, are not considered.

1. *Steady Mean Lag of a Metallic Thermometer.*

The steady lag in the mean temperature of a thermometer may be written in the form

$$G\rho\sigma\left(\frac{M}{K}+\frac{N}{h}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where G is the constant temperature-time gradient in the medium, ρ is the density, σ the specific heat, K the thermal conductivity, and h the surface conductivity of the thermometric substance, and M and N are constants whose values depend upon the shape and dimensions of the bulb.

Under certain circumstances the internal lag, which is represented by the first term in (1), may be neglected leaving only the surface lag, represented by the second term and due to the passage of heat across the surface, to be considered. This may be done if K is large compared with h, which is the case for most metals used in air or some other medium in which the value of h is not too great. It may also be done if one of the dimensions of the thermometers is very small, since M depends upon the square of the linear dimensions while N depends only upon the first power. In such cases the steady lag may be written in the form

$$NG\rho\sigma/h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and the value of N is given by the ratio

$$N=\frac{\text{volume of thermometer}}{\text{area of exposed surface}}. \quad . \quad . \quad . \quad (3)$$

It is easily seen that this ratio must occur as a factor in N; for the surface conductivity term only takes account of the passage of heat across the surface, and if the area is doubled, the heat is lost or gained twice as rapidly and so the lag is halved; while if the volume is doubled, there is twice as much heat to be lost or gained and so the lag is doubled. Any other non-dimensional factor must be unity, since $N=c/3$ for a sphere, and $c/2$ for a cylinder, c being the radius.

2. *Case of a Cylindrical Bulb.* (Infinite Length.)

If $a^2=K/\rho\sigma$, we require a solution of

$$\frac{1}{a^2}\frac{\partial u}{\partial t}=\frac{1}{r}\frac{\partial u}{\partial r}+\frac{\partial^2 u}{\partial r^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which satisfies the conditions

$$u=F(r) \text{ for } t=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{K}{h}\frac{\partial u}{\partial r}+u=\phi(t) \text{ for } r=c, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

c being the radius of the cylinder, u the temperature, and t the time.

The solution satisfying condition (6) is given by Fourier in his *Théorie Analytique de la Chaleur*, p. 309. The following treatment is set out here, however, as it is much more concise than Fourier's * and follows different lines. The general solution of the form required is

$$u=\sum_{n=1}^{\infty} A_n J_0(\alpha_n r/c)e^{-a^2\alpha_n^2 t/c^2}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where A_n and α_n are arbitrary constants to be determined by the conditions, and J_0 is the Bessel function of zero order.

The basis of the solutions is the well-known expansion (*cf.* Whittaker, 'Modern Analysis,' p. 374, Ex. 20)

$$f\left(\frac{r}{c}\right)=\sum_{n=1}^{\infty} J_0(\beta_n r/c)\frac{\int_0^1 \xi f(\xi)J_0(\beta_n\xi)d\xi}{\int_0^1 \xi\{J_0(\beta_n\xi)\}^2 d\xi}, \quad . \quad . \quad . \quad (8)$$

where

$$\beta_n J_0'(\beta_n)+HJ_0(\beta_n)=0, \qquad H=ch/K. \quad . \quad . \quad (9)$$

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* See also, Carslaw, 'Introduction to the Theory of Fourier's Series and Integrals,' p. 208.

Take $f(r/c)=1$. Then, since

$$\int_0^1 \xi J_0(\beta_n\xi)\,d\xi = HJ_0(\beta_n)\,/\,\beta_n^2,$$

$$\int_0^1 \xi\{J_0(\beta_n)\}^2 d\xi = (\beta_n^2+H^2)\{J_0(\beta_n)\}^2/2\beta_n^2,$$

we have

$$1=\sum_{n=1}^{\infty}\frac{2HJ_0(\beta_n r/c)}{(\beta_n^2+H^2)J_0(\beta_n)}. \quad . \quad . \quad . \quad . \quad (10)$$

Write

$$\chi(r,t)=1-\sum_{n=1}^{\infty}\frac{2HJ_0(\beta_n r/c)}{(\beta_n^2+H^2)J_0(\beta_n)}e^{-a^2\beta_n^2t/c^2},\ t>0$$

$$\chi(r,t)=0, \qquad t\leq 0.$$

Consider, for $t>0$,

$$\psi(r,t)=1+H\left(\frac{c}{r}-1\right)\sum_{n=1}^{\infty}\frac{2J_0(\beta_n r/c)e^{-a^2\beta_n^2t/c^2}}{(\beta_n^2+H^2)J_0(\beta_n)}.$$

We see that

$$\psi(c,t)=1, \qquad t>0,$$

and we define

$$\psi(c,t)=0, \qquad t\leq 0.$$

Further, as $r\rightarrow c$, the ratio of $\psi(r,t)-1$ to $\frac{c}{H}\frac{\partial\chi}{\partial r}+\chi-1$ tends to unity.

Now by the usual method *, the function

$$\int_0^t \phi(\tau)\frac{\partial\psi(r,t-\tau)}{\partial t}d\tau$$

reduces to the value $\phi(t)$ when $r=c$. Performing the differentiation, this becomes

$$\frac{2a^2H}{c^2}\left(1-\frac{c}{r}\right)\sum_{n=1}^{\infty}\frac{\beta_n^2J_0(\beta_n r/c)e^{-a^2\beta_n^2t/c^2}}{(\beta_n^2+H^2)J_0(\beta_n)}\int_0^t\phi(\tau)e^{a^2\beta_n^2\tau/c^2}d\tau.$$

Hence, by inspection, the solution corresponding to χ, which is the one we require for condition (6), is the second of the terms on the right of (11), and the solution we require is

$$\left.\begin{aligned} u=&\sum_{n=1}^{\infty}\frac{2\beta_n^2J_0(\beta_n r/c)e^{-a^2\beta_n^2t/c^2}}{(\beta_n^2+H^2)\{J_0(\beta_n)\}^2}\int_0^1\xi F(c\xi)J_0(\beta_n\xi)d\xi \\ &+\frac{2a^2H}{c^2}\sum_{n=1}^{\infty}\frac{\beta_n^2J_0(\beta_n r/c)e^{-a^2\beta_n^2t/c^2}}{(\beta_n^2+H^2)J_0(\beta_n)}\int_0^t\phi(\tau)e^{a^2\beta_n^2\tau/c^2}d\tau \end{aligned}\right\}. \quad (11)$$

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* Phil. Mag. Jan. 1919, or Weber, *Partielle Differentialgleichungen*, Band ii.

As a special case take $F(r)=u_0=$constant, and $\phi(t)=Gt$, where G is a constant. Then the solution becomes

$$\left.\begin{aligned} u = &\sum_{n=1}^{\infty}\frac{2u_0 H J_0(\beta_n r/c)}{(\beta_n^2+H^2)J_0(\beta_n)}e^{-a^2\beta_n^2 t/c^2} \\ &+\sum_{n=1}^{\infty}\frac{2GHJ_0(\beta_n r/c)}{(\beta_n^2+H^2)J_0(\beta_n)}\left\{t+\frac{c^2}{a^2\beta_n^2}(e^{-a^2\beta_n^2 t/c^2}-1)\right\}\end{aligned}\right\} . \quad (12)$$

To evaluate the series which occur, we equate the expansions of $xJ_0'((x)+HJ_0(x)$ as an infinite product and as an infinite series.

$$H\prod_{n=1}^{\infty}\left(1-\frac{x^2}{\beta_n^2}\right)=H\left[1-x^2\left(\frac{1}{4}+\frac{1}{2H}\right)+x^4\left(\frac{1}{64}+\frac{1}{16H}\right)-\ldots\right]. \quad . \quad . \quad . \quad (13)$$

Writing $r=c$ in (10), we get

$$\sum_{n=1}^{\infty}\frac{2H}{\beta_n^2+H^2}=1, \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and with the aid of (14) we find, after equating coefficients in (13),

$$\sum_{n=1}^{\infty}\frac{4H^2}{\beta_n^2(\beta_n^2+H^2)}=1, \qquad \sum_{n=1}^{\infty}\frac{4H^2}{\beta_n^4(\beta_n^2+H^2)}=\frac{1}{8}+\frac{1}{2H}.$$

Taking the mean temperature we find from (12) the value for the mean lag

$$\frac{Gc^2}{a^2}\left(\frac{1}{8}+\frac{1}{2H}\right)-\sum_{n=1}^{\infty}\frac{4H^2e^{-a^2\beta_n^2t/c^2}}{\beta_n^2(\beta_n^2+H^2)}\left(u_0+\frac{Gc^2}{a^2\beta_n^2}\right). \quad (15)$$

On writing $u_0=0$, we get the lag given by Dr. Bromwich's formula.

In the next case to be considered, we have the solution (12) until $t=t_1$, when the surface condition becomes

$$\phi(t)=Gt_1+G'(t-t_1) \text{ for } t>t_1. \quad . \quad . \quad . \quad (16)$$

Writing $t'=t-t_1$, we have, after time t_1, a new problem in which the conditions are

$$\left.\begin{aligned} F(r)=&\sum_{n=1}^{\infty}\frac{2HJ_0(\beta_n r/c)}{(\beta_n^2+H^2)J_0(\beta_n)}\left[u_0e^{-a^2\beta_n^2t_1/c^2}\right. \\ &\qquad\left.+G\left\{t_1+\frac{c^2}{a^2\beta_n^2}(e^{-a^2\beta_n^2t_1/c^2}-1)\right\}\right] \\ \phi(t)=&\,Gt_1+G't'.\end{aligned}\right\} . \quad (17)$$

Substituting in (11), we find, since the series are uniformly convergent,

$$u = \mathrm{G}t_1 + \mathrm{G}'t' - \sum_{n=1}^{\infty} \frac{2\mathrm{HJ}_0(\beta_n r/c)}{(\beta_n^2 + \mathrm{H}^2)\mathrm{J}_0(\beta_n)} \left[\frac{(\mathrm{G}-\mathrm{G}')c^2}{a^2\beta_n^2} e^{-a^2\beta_n^2 t'/c^2} + \frac{\mathrm{G}'c^2}{a^2\beta_n^2} - \left(u_0 + \frac{\mathrm{G}c^2}{a^2\beta_n^2}\right) e^{-a^2\beta_n^2 t/c^2} \right]. \quad . \quad (18)$$

Taking the mean temperature, we get for the mean lag

$$\mathrm{L} = \frac{\mathrm{G}'c^2}{a^2}\left(\frac{1}{8} + \frac{1}{2\mathrm{H}}\right) + \sum_{n=1}^{\infty} \frac{4\mathrm{H}^2}{\beta_n^2(\beta_n^2 + \mathrm{H}^2)} \left[\frac{(\mathrm{G}-\mathrm{G}')c^2}{a^2\beta_n^2} e^{-a^2\beta_n^2 t'/c^2} - \left(u_0 + \frac{\mathrm{G}c^2}{a^2\beta_n^2}\right) e^{-a^2\beta_n^2 t/c^2} \right]. \quad . \quad (19)$$

3. *Case of a Spherical Bulb.*

To preserve the analogy, the solution will be obtained by the use of Bessel functions. We require a solution, satisfying conditions (5) and (6) (in which c is now the radius of the sphere) of the equation

$$\frac{1}{a^2}\frac{\partial u}{\partial t} = \frac{2}{r}\frac{\partial u}{\partial r} + \frac{\partial^2 u}{\partial r^2}. \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Substituting $u = r^{-\frac{1}{2}} v e^{-a^2\alpha_n^2 t/c^2}$, $x = \alpha_n r/c$, we get

$$\frac{d^2 v}{dx^2} + \frac{1}{x}\frac{dv}{dx} + \left(1 - \frac{1}{4x^2}\right)v = 0.$$

Hence the general solution of (20) of the type required is

$$u = \sum_{n=1}^{\infty} \mathrm{A}_n r^{-\frac{1}{2}} \mathrm{J}_{\frac{1}{2}}(\alpha_n r/c)\, e^{-a^2\alpha_n^2 t/c^2}. \quad . \quad . \quad . \quad (21)$$

To determine the constants α_n, we arrive at the condition

$$\alpha_n \mathrm{J}_{\frac{1}{2}}'(\alpha_n) + (\mathrm{H} - \tfrac{1}{2})\mathrm{J}_{\frac{1}{2}}(\alpha_n) = 0, \quad . \quad . \quad . \quad (22)$$

or

$$(1 - \mathrm{H}) \tan \alpha_n = \alpha_n.$$

The basic expansion is

$$f\left(\frac{r}{c}\right) = \sum_{n=1}^{\infty} \left(\frac{r}{c}\right)^{-\frac{1}{2}} \mathrm{J}_{\frac{1}{2}}(\alpha_n r/c) \frac{\int_0^1 \xi^{\frac{3}{2}} f(\xi) \mathrm{J}_{\frac{1}{2}}(\alpha_n \xi)\, d\xi}{\int_0^1 \xi \{\mathrm{J}_{\frac{1}{2}}(\alpha_n \xi)\}^2 d\xi}, \qquad (23)$$

and since

$$\int_0^1 \xi^{\frac{3}{2}} J_{\frac{1}{2}}(\alpha_n\xi)\,d\xi = HJ_{\frac{1}{2}}(\alpha_n)/\alpha_n^2,$$

$$\int_0^1 \xi\{J_{\frac{1}{2}}(\alpha_n)\}^2 d\xi = \{\alpha_n^2+H(H-1)\}\{J_{\frac{1}{2}}(\alpha_n)\}^2/2\alpha_n^2,$$

we have, calling the constant coefficient A_n,

$$1=\sum_{n=1}^{\infty}\frac{2H(r/c)^{-\frac{1}{2}}J_{\frac{1}{2}}(\alpha_n r/c)}{\{\alpha_n^2+H(H-1)\}J_{\frac{1}{2}}(\alpha_n)} = \sum_{n=1}^{\infty} A_n(r/c)^{-\frac{1}{2}}J_{\frac{1}{2}}(\alpha_n r/c). \qquad (24)$$

Defining $\chi(r, t)$ to be zero for $t<0$, and

$$\chi(r, t)=1-\sum_{n=1}^{\infty} A_n(r/c)^{-\frac{1}{2}}J_{\frac{1}{2}}(\alpha_n r/c)e^{-a^2\alpha_n^2t/c^2}, \quad t>0,$$

we have for the function $\psi(r, t)$, when $t>0$,

$$\psi(r, t)=1-\sum_{n=1}^{\infty} A_n(r/c)^{-\frac{1}{2}}e^{-a^2\alpha_n^2t/c^2}\Big[J_{\frac{1}{2}}(\alpha_n r/c) + \frac{1}{H}\Big\{-\frac{c}{2r}J_{\frac{1}{2}}(\alpha_n r/c)+\alpha_n J_{\frac{1}{2}}'(\alpha_n r/c)\Big\}\Big]$$

And, as before, the function which takes the value $\phi(t)$ for $r=c$ is given by

$$\sum_{n=1}^{\infty}\frac{A_n a^2\alpha_n^2e^{-a^2\alpha_n^2t/c^2}}{c^2(r/c)^{\frac{1}{2}}}\Big[J_{\frac{1}{2}}(\alpha_n r/c) + \frac{1}{H}\Big\{-\frac{c}{2r}J_{\frac{1}{2}}(\alpha_n r/c)+\alpha_n J_{\frac{1}{2}}'(\alpha_n r/c)\Big\}\Big]\int_0^t \phi(\tau)e^{a^2\alpha_n^2\tau/c^2}d\tau.$$

The solution for u satisfying (6) is then found to be the second term on the right of (25), and the solution required is

$$\left.\begin{aligned} u &= \sum_{n=1}^{\infty}\frac{2\alpha_n^2e^{-a^2\alpha_n^2t/c^2}}{\{\alpha_n^2+H(H-1)\}\{J_{\frac{1}{2}}(\alpha_n)\}^2}\,\frac{J_{\frac{1}{2}}(\alpha_n r/c)}{(r/c)^{\frac{1}{2}}}\int_0^1 \xi^{\frac{3}{2}}F(c\xi)J_{\frac{1}{2}}(\alpha_n\xi)d\xi \\ &+ \sum_{n=1}^{\infty}\frac{2Ha^2\alpha_n^2e^{-a^2\alpha_n^2t/c^2}}{c^2\{\alpha_n^2+H(H-1)\}J_{\frac{1}{2}}(\alpha_n)}\,\frac{J_{\frac{1}{2}}(\alpha_n r/c)}{(r/c)^{\frac{1}{2}}}\int_0^t \phi(\tau)e^{a^2\alpha_n^2\tau/c^2}d\tau. \end{aligned}\right\} \qquad (25)$$

Taking $F(r)=u_0$, and $\phi(t)=Gt$, we get

$$\left.\begin{aligned} u &= \sum_{n=1}^{\infty}\frac{2u_0H(r/c)^{-\frac{1}{2}}J_{\frac{1}{2}}(\alpha_n r/c)}{\{\alpha_n^2+H(H-1)\}J_{\frac{1}{2}}(\alpha_n)}e^{-a^2\alpha_n^2t/c^2} \\ &+ \sum_{n=1}^{\infty}\frac{2GH(r/c)^{-\frac{1}{2}}J_{\frac{1}{2}}(\alpha_n r/c)}{\{\alpha_n^2+H(H-1)\}J_{\frac{1}{2}}(\alpha_n)}\Big\{t+\frac{c^2}{a^2\alpha_n^2}(e^{-a^2\alpha_n^2t/c^2}-1)\Big\}. \end{aligned}\right\} \qquad (26)$$

Using the series

$$\sum_{n=1}^{\infty}\frac{2\text{H}}{\alpha_n{}^2+\text{H}(\text{H}-1)}=1=\sum_{n=1}^{\infty}\frac{6\text{H}^2}{\alpha_n{}^2\{\alpha_n{}^2+\text{H}(\text{H}-1)\}}$$

$$\sum_{n=1}^{\infty}\frac{6\text{H}^2}{\alpha_n{}^4\{\alpha_n{}^2+\text{H}(\text{H}-1)\}}=\frac{1}{15}+\frac{1}{3\text{H}},$$

we find for the lag in the mean temperature

$$\frac{\text{G}c^2}{a^2}\left(\frac{1}{15}+\frac{1}{3\text{H}}\right)-\sum_{n=1}^{\infty}\frac{6\text{H}^2e^{-a^2\alpha_n{}^2t/c^2}}{\alpha_n{}^2\{\alpha_n{}^2+\text{H}(\text{H}-1)\}}\left(u_0+\frac{\text{G}c^2}{a^2\alpha_n{}^2}\right). \quad (27)$$

On writing $u_0=0$, we get the lag given by Dr. Bromwich's formula.

In the case of the temperature inversion, in which the solution (26) holds until $t=t_1$, and new conditions then set in, the initial condition being given by writing $t=t_1$ in (26), and the surface condition by (16), we find without difficulty

$$u=\text{G}t_1+\text{G}'t'-\sum_{n=1}^{\infty}\frac{2\text{H}(r/c)^{-\frac{1}{2}}\text{J}_{\frac{1}{2}}(\alpha_nr/c)}{\{\alpha_n{}^2+\text{H}(\text{H}-1)\}\text{J}_{\frac{1}{2}}(\alpha_n)}\left[\frac{(\text{G}-\text{G}')c^2}{a^2\alpha_n{}^2}e^{-a^2\alpha_n{}^2t'/c^2}\right.$$
$$\left.+\frac{\text{G}'c^2}{a^2\alpha_n{}^2}-\left(u_0+\frac{\text{G}c^2}{a^2\alpha_n{}^2}\right)e^{-a^2\alpha_n{}^2t/c^2}\right]. \quad . \quad (28)$$

The lag of the mean temperature is found to be

$$\text{L}=\text{G}'\frac{c^2}{a^2}\left(\frac{1}{15}+\frac{1}{3\text{H}}\right)+\sum_{n=1}^{\infty}\frac{6\text{H}^2}{\alpha_n{}^2\{\alpha_n{}^2+\text{H}(\text{H}-1)\}}\left[\frac{(\text{G}-\text{G}')c^2}{a^2\alpha_n{}^2}e^{-a^2\alpha_n{}^2t'/c^2}\right.$$
$$\left.-\left(u_0+\frac{\text{G}c^2}{a^2\alpha_n{}^2}\right)e^{-a^2\alpha_n{}^2t/c^2}\right]. \quad . \quad (29)$$

4. *Numerical Results.*

We consider the same bulbs that were dealt with in the former paper (Phil. Mag. Jan. 1919). These have the same sensitiveness for a given thermometer stem, the expansion of alcohol being taken as six times that of mercury. Particulars are given below.

The surface conductivity is taken from the same paper and is given (in C.G.S. units) by

$$h=\cdot 0000515\,\text{V}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

The air density for which (30) holds is that near the ground, V being the velocity of the aeroplane in miles per hour. The data on which this value is based were obtained from work on radiators and engine cooling done at the Royal

Aircraft Establishment. As a rough check, values of h were calculated from the cooling of mercury and alcohol thermometers in the Wind Channel, the air velocity being 34 m.p.h. The value obtained from the cooling of the mercury thermometer ($c=1$ cm. nearly) for the constant in (30) was about ·000047, and the alcohol sphere ($c=\cdot 5$ cm.) yielded a value nearly equal to ·0001, but the result was much less reliable than that with the mercury thermometer as only one term of the series was used in the calculation.

For convenience the symbols used below are collected here with their meanings.

u_0 = initial constant temperature of thermometer.
V = velocity of wind past the thermometer in miles per hour.
h = surface conductivity of thermometer bulb.
K = thermal conductivity of thermometric substance.
ρ = density of thermometric substance.
σ = specific heat of thermometric substance.
$a^2 = K/\rho\sigma$.
c = radius of sphere or cylinder (inner radius of glass bulb).
$H = ch/K$.
G = temperature-time gradient before the temperature inversion (time $=t$).
G' = temperature-time gradient after inversion (time $=t' = t-t_1$.)
α_1, β_1, α_2, etc. are constants occurring in formulæ (19) and (29) which give the mean lags.
L_1, L_2, L_3, are lags occurring with the pairs of values of G and G' which are given below.

The following data are given :—

$u_0 = 5°$ C. $V = 70$ m.p.h. $h = \cdot 00360$.

Mercury. (At temperature 15°–20° C.)

$K = \cdot 0197$ $a^2 = \cdot 0437$.
Sphere : $c = 1$ cm. $H = \cdot 183$
$\alpha_1 = \cdot 7276$ $\alpha_2 = 4\cdot 534$.
Cylinder : $c = \cdot 365$ cm. $H = \cdot 0667$
(10 cm. long) $\beta_1 = \cdot 3622$ $\beta_2 = 3\cdot 849$.

Alcohol.

$K = \cdot 00043$ $a^2 = \cdot 000903$.
Sphere : $c = \cdot 550$ cm. $H = 4\cdot 65$
$\alpha_1 = 2\cdot 5351$ $\alpha_2 = 5\cdot 314$ $\alpha_3 = 8\cdot 270$.
Cylinder : $c = \cdot 149$ cm. $H = 1\cdot 248$
(10 cm. long) $\beta_1 = 1\cdot 365$ $\beta_2 = 4\cdot 136$.

Substituting in the formulæ (19) and (29), we have the values of the lags in the mean temperature of the bulbs which are given below. The temperatures are in degrees centigrade, the times in seconds, and t_1 is large so that the inversion occurs only when the steady lag on the first gradient has been attained. If $t<t_1$, we write $t'=0$ in the two formulæ. The two gradients used, viz.: $G=\cdot028°$ C./sec., and $G'=\cdot185°$ C./sec., correspond to temperature gradients of 1°·68 C. and 11°·10 C. per thousand feet of height (5°·5 C. and 36·7° C. per km.), and a rate of climb of 1000 feet per minute. In the case of a cylindrical bulb, the length need only be sufficient to enable the effects of the ends to be neglected. Formula (19) is then applicable.

Mercury Sphere.

When $G=\cdot028$ the steady lag is 1°·21 C.
$G'=\cdot185$ „ „ „ „ 8°·00 C.

(i.) When $G=\cdot028$ and $G'=-\cdot185$,

$$L_1=-8{\cdot}00-6{\cdot}22\,e^{-\cdot0231t}+9{\cdot}22\,e^{-\cdot0231t'}. \qquad (31)$$

(ii.) When $G=-\cdot028$ and $G'=+\cdot185$,

$$L_2=8{\cdot}00-3{\cdot}79^{-\cdot0231t}-9{\cdot}22\,e^{-\cdot0231t'}. \qquad (32)$$

(iii.) When $G=-\cdot028$ and $G'=+\cdot028$,

$$L_3=1{\cdot}21-3{\cdot}79\,e^{-\cdot0231t}-2{\cdot}42\,e^{-\cdot0231t'}. \qquad (33)$$

Curves are plotted in fig. 1, the straight lines representing true temperatures.

Alcohol Sphere.

When $G=\cdot028$ the steady lag is 1°·29 C.
„ $G=\cdot185$ „ „ „ „ 8°·57 C.

The lags in the three cases considered above are:

$$\left.\begin{aligned}L_1=&-8{\cdot}57-5{\cdot}57\,e^{-\cdot0192t}-\cdot54\,e^{-\cdot084t}-\cdot11\,e^{-\cdot205t}\\&+9{\cdot}59\,e^{-\cdot0192t'}+\cdot26\,e^{-\cdot084t'}+\cdot02\,e^{-\cdot205t'},\end{aligned}\right\} \qquad (34)$$

$$\left.\begin{aligned}L_2=&\,8{\cdot}57-3{\cdot}06\,e^{-\cdot0192t}-\cdot47\,e^{-\cdot084t}-\cdot11\,e^{-\cdot205t}\\&-9{\cdot}59\,e^{-\cdot0192t'}-\cdot26\,e^{-\cdot084t'}-\cdot02\,e^{-\cdot205t'}.\end{aligned}\right\} \qquad (35)$$

$$\left.\begin{aligned}L_3=&\,1{\cdot}29-3{\cdot}06\,e^{-\cdot0192t}-\cdot47\,e^{-\cdot084t}-\cdot11\,e^{-\cdot205t}\\&-2{\cdot}52\,e^{-\cdot0192t'}-\cdot07\,e^{-\cdot084t}-\cdot01\,e^{-\cdot205t'}.\end{aligned}\right\} \qquad (36)$$

Mercury Cylinder.

When $G = \cdot 028$ the steady lag is ·65° C.
,, $G = \cdot 185$,, ,, ,, ,, 4°·30 C.

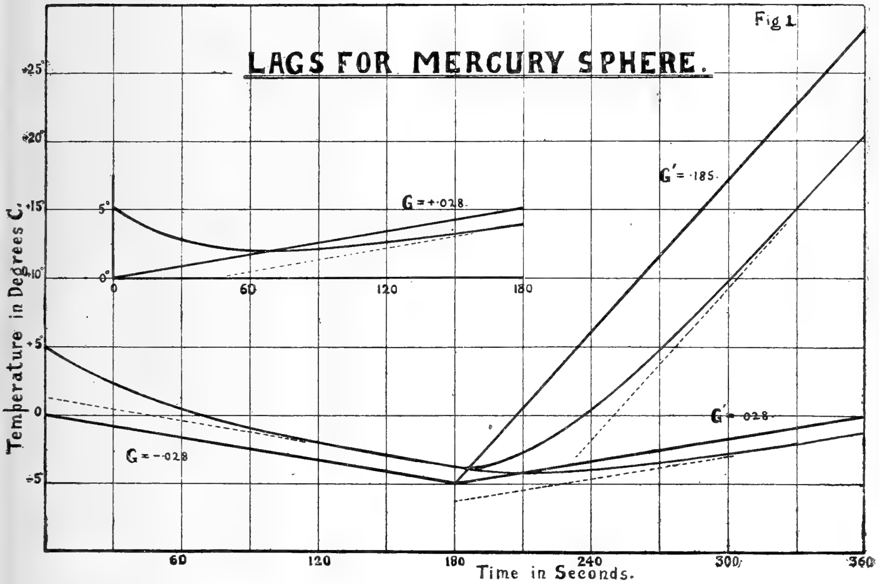
The lags in the three cases considered are :

$$L_1 = -4\cdot 30 - 5\cdot 65\, e^{-\cdot 0430t} + 4\cdot 95\, e^{-\cdot 0430t'}, \quad \ldots \quad (37)$$

$$L_2 = 4\cdot 30 - 4\cdot 35\, e^{-\cdot 0430t} - 4\cdot 95\, e^{-\cdot 0430t'}, \quad \ldots \quad (38)$$

$$L_3 = \cdot 65 - 4\cdot 35\, e^{-\cdot 0430t} - 1\cdot 30\, e^{-\cdot 0430t'}, \quad \ldots \quad (39)$$

Fig. 1.



Alcohol Cylinder.

When $G = \cdot 028$ the steady lag is ·36° C.
,, $G = \cdot 185$,, ,, ,, ,, 2·39° C.

The lags in the three cases considered are :

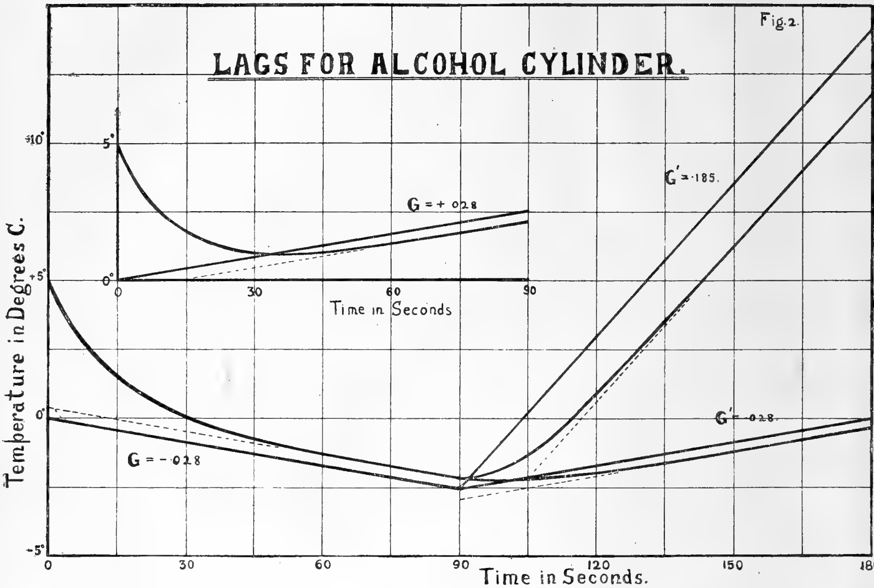
$$L_1 = -2\cdot 39 - 5\cdot 25\, e^{-\cdot 0758t} + 2\cdot 75\, e^{-\cdot 0758t'}, \quad \ldots \quad (40)$$

$$L_2 = 2\cdot 39 - 4\cdot 67\, e^{-\cdot 0758t} - 2\cdot 75\, e^{-\cdot 0758t'}, \quad \ldots \quad (41)$$

$$L_3 = \cdot 36 - 4\cdot 67\, e^{-\cdot 0758t} - \cdot 72\, e^{-\cdot 0758t'}. \quad \ldots \quad (42)$$

Curves are plotted in fig. 2.

Fig. 2.



Hence from these values and the curves in figs. 1 and 2, we see that cylinders of the dimensions given are much superior to spheres, and the alcohol cylinder is the best of the four *. The times taken for the temperature to drop from 5° C. (when $t=0$) to within a given fraction of the steady lag are approximately proportional to the values of the steady lags, so that the steady lags alone will suffice to compare the rates of response of two thermometers to outside temperature changes. For example, the times taken to drop to half the steady lags are respectively 100^s, 112^s, 67^s, and 44^s nearly.

The effect of the glass will be to increase the value of c. If the thickness of the glass wall is a small fraction of the inner radius, which we have taken as c, the correction should be a fraction of the same order, and the lags will be similarly affected.

At the point of inversion, the lag changes continuously from its value at time t_1 to the steady value on the new gradient. Hence the greatest error in the thermometer reading cannot exceed the greater of the two steady lags.

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* See however para. 5.

Any number of successive inversions of the type considered can be combined, and the exact solution, analogous to (19) and (29), is easily obtained. Unless the inversions are of very short duration, the approximate lag can be deduced from the steady lags on the various gradients without much trouble.

5. *Effect of Varying the Bore of the Capillary Tube.*

The steady lag of a thermometer is given by (1), where M has the dimensions of c^2, being equal to $c^2/15$ for the sphere, and $c^2/8$ for the cylinder ; and N has the dimensions of c, being equal to $c/3$ for the sphere and $c/2$ for the cylinder. The four examples of liquid thermometers we considered in para. 4, all gave the same accuracy of reading (same openness of scale) when used with the same thermometer stem. If the area of section of the capillary tube is multiplied by a factor μ, the volume of the bulb must be multiplied by the same factor to retain the previous accuracy of reading. Hence for the new spherical bulb the radius is $c'=\mu^{\frac{1}{3}}c$, while for the new cylinder the radius is $(\mu l/l')^{\frac{1}{2}}c$, l' being the new length, and l the previous length of the cylinder. The lags of the new thermometers, all of which have the same accuracy when used with the new stem, are therefore

$$\mathrm{G}\rho\sigma\left(\frac{c^2\mu^{\frac{2}{3}}}{15\mathrm{K}}+\frac{c\mu^{\frac{1}{3}}}{3h}\right) \quad . \quad . \quad . \quad . \quad . \quad (43)$$

for the new sphere of radius $c\mu^{\frac{1}{3}}$; and

$$\mathrm{G}\rho\sigma\left(\frac{c^2\mu l}{8\mathrm{K}l'}+\frac{c}{2h}\left(\frac{\mu l}{l'}\right)^{\frac{1}{2}}\right) \quad . \quad . \quad . \quad . \quad . \quad (44)$$

for the new cylinder of radius $c\sqrt{\mu l/l'}$. Now the lag of the cylinder is not affected appreciably, so long as the cross-section is small in comparison with the length, by varying l. Hence if we choose a new length for the cylinder such that $l'=\mu l$, the lag (44) has still the previous value. If l' has a greater value than μl the lag will be diminished because the new radius c' must be less than c. For the sphere, however, the lag will always be less when $\mu<1$, and *vice versa*.

Commencing anew, let us suppose that the bulbs considered in para. 4 are all used in conjunction with a stem, which has the smallest practicable capillary tube that may be used with alcohol. For mercury, a much smaller bore is still possible. Let us now designate by μ the ratio of areas of the sections of the smallest capillary tubes practicable for mercury and alcohol. Then, owing to this further reduction in bore in the case of mercury, the lags for mercury are given by the expressions (43) and (44), while the lags for alcohol have the values

$$G\rho\sigma\left(\frac{c^2}{15K}+\frac{c}{3h}\right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (45)$$

for the sphere of radius c; and

$$G\rho\sigma\left(\frac{c^2}{8K}+\frac{c}{2h}\right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (46)$$

for the cylinder of radius c.

But for mercury we may neglect the first terms in (43) and (44), and so these lags become

For the mercury sphere $G\rho\sigma c\mu^{\frac{1}{3}}/3h$, . . (47)

" " " cylinder $\dfrac{G\rho\sigma c}{2h}\sqrt{\dfrac{\mu l}{l'}}$ . . . (48)

Messrs. Pastorelli & Rapkin of Hatton Garden state that fine capillary tubes, when used with alcohol, must have a circular section as otherwise the meniscus is distorted. The limiting diameter of capillary which may be used they give as ·25 mm., while ·50 mm. would be a good working limit. Mercury thermometers, on the other hand, can apparently be made with the finest capillary tubes that can be drawn. Two samples of ordinary small clinical thermometers, supplied by Messrs. Pastorelli & Rapkin, were broken across half-way up the stem, and the capillary tube was measured under the microscope. In one the elliptical tube had dimensions ·10 mm. × ·031 mm. with a sectional area of ·0025 sq. mm. In the other, the dimensions were ·063 mm. and ·043 mm. and the area was ·0021 sq. mm.

James J. Hicks of Hatton Garden supplied samples of alcohol and mercury thermometer tubes having a glass wall of irregular thickness, suitable for magnifying the diameter of the capillary tube and so enabling readings to be taken at a distance. The alcohol tube had a circular bore of 1·0 mm. diameter and is used in the Strutt Thermometers supplied to the R.A.F. The mercury tube had a circular bore of ·125 mm. diameter. This was stated to be the smallest practicable mercurial bore (presumably with this type of magnifying stem). The ratio of the sections of these specimens is 64 : 1.

Taking ·002 sq. mm. as the smallest section of capillary tube for a mercury thermometer, and ·203 sq. mm. (diameter =·50 mm.) as the smallest section for an alcohol thermometer, we find the value $\mu=1/100$. While if the smallest area for the alcohol thermometer is ·0506 sq. mm. (diameter =·25 mm.) we find $\mu=1/25$. The corresponding values of $\mu^{\frac{1}{3}}$ are 1/4·6 and 1/2·9. Hence, by taking the smallest possible bores for the capillary tubes in the thermometer stems, the accuracy of reading remaining the same for all thermometers throughout, it is possible to reduce the lags for a mercury sphere by a factor whose value is of the order 1/5 to 1/3, when the lag for the alcohol sphere has reached its lowest possible value, consistent with the particular accuracy of reading, *i.e.* linear scale, required.

Accordingly, if we are seeking to determine the thermometer with the least possible lag consistent with the accuracy obtainable with an alcohol sphere of radius ·550 cm. and a capillary tube of bore ·50 mm. diameter, the lags obtained with mercury in para. 4 must be multiplied by a factor ·2 in the case of the sphere, and ·1 in the case of the cylinder. The mercury cylinder would thus be the best possible with a lag of ·07 for G=·028° C./sec. The mercury sphere would have a least possible lag of ·24° C., which is less than the least possible lag for the alcohol cylinder of ·36° C. Of course these very fine capillary tubes may be very objectionable for various purposes, owing to difficulty in reading readily, or for some other reason. The point which is here emphasized, however, is that the possibility exists of making mercury thermometers with much less lag than alcohol thermometers which have the same linear scale. If the same capillary tube is used with equivalent bulbs, the conclusions of para. 4 stand, and the alcohol cylinder has the least lag. A further variation may occur when the accuracy of reading (linear scale) is changed. This has not been considered.

6. *Bimetallic Thermometers.*

As an example of the application of formulæ (2) and (3), the case of a bimetallic recording thermometer by Pastorelli & Rapkin may be considered. In this instrument the pen is moved across a rotating cylinder by the relative thermal expansion of two strips of aluminium and brass, secured face to face. Each strip was 29 cm. long, 1·15 cm. wide, and ·09 cm. thick. Hence for each strip,

$$\mathrm{N}=\frac{1{\cdot}15\times{\cdot}09}{1{\cdot}15+{\cdot}18}={\cdot}078 \text{ (approx.)}.$$

For aluminium $\rho\sigma = \cdot 53$; and for brass $\rho\sigma = \cdot 75$.
Taking $G = \cdot 028°$ C./sec., and $h = \cdot 00360$,

lag for aluminium strip = ·32° (approx.),
" " brass " = ·45° "

Hence the lag for the thermometer will be about ·38° C. when the temperature change is at the rate of 1° C. in 36 seconds. If steel were substituted for the brass the pen motion would be about doubled, and the lag would be increased to about ·45° C.

The lag is not reduced by varying the length or breadth of the metal strips (provided these are large in comparison with the thickness), but only by making them thinner. A second bimetallic thermometer, by Short & Mason, consisted of a double strip of brass and steel rolled spirally in the form of a cylindrical tube. The width of the strip was ·5 cm. The steel was ·03 cm. thick and the brass ·07 cm. The lag, when $G = \cdot 028$, for the steel strip is ·16°, and for the brass ·37° C.; so the thermometer would have a mean lag of about ·30° C.

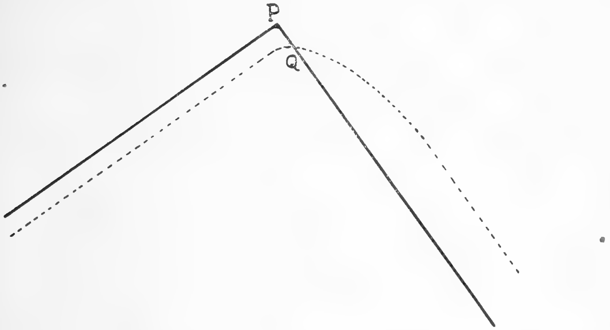
As a further example, consider the case of the Dines "ballon sonde" thermometer. In this instrument the pen is supported at one point by an invar tube, and at a second point by a german-silver strip ·02 cm. thick and about ·5 cm. wide. The lag of the invar is immaterial. For the german-silver strip $\rho\sigma = \cdot 84$, and the value of N in formula (2) is simply half the thickness, viz.: $N = \cdot 01$. Hence the lag of the thermometer is $\cdot 0084\, G/h$. If $G = \cdot 028°$ C./sec. and $h = \cdot 00360$ the lag is ·065° C. But if the thermometer is carried by a balloon ascending at the rate of 750 feet per minute, $V = 8 \cdot 5$ m.p.h., and from (30) we get $h = \cdot 00044$. Then if the lapse rate is 1°·68 C. per thousand feet (5°·5 C. per km.) the lag is ·40° C. We do not consider here the variation of surface conductivity with air density.

In the same case ($h = \cdot 00044$) the lag of a Teisserenc de Bort thermometer as used at Trappes has a mean lag of 1°·73 C. The bimetallic strip has dimensions ·11 cm. × ·62 cm. × 11·0 cm. and consists of brass and iron, the thicknesses being in the ratio 3 : 2.

7. *Displacement of Temperature Maximum due to Lag.*

One of the effects of lag is to displace the position of the maximum or minimum reading of the thermometer from the true time-position on the chart. Suppose the temperature inversion in the accompanying figure is under consideration, times being measured to the right, and temperature

Fig. 3.



towards the top. On the left, the temperature is increasing at the constant rate G, shown by the full line, and the thermometer reading lags behind, as shown by the dotted line. After the inversion at P, the air temperature decreases at the constant rate G′, shown by the full line on the right. The true maximum is at P, but the thermometer maximum is at Q, where the dotted line crosses the second straight line. In the neighbourhood of P, the lag is given by formula (19)—in the case of the cylinder—and we have on writing $t=\infty$ in that formula, and retaining only the first term of the series,

$$L=\frac{G'c^2}{a^2}\left(\frac{1}{8}+\frac{1}{2H}\right)+\frac{4H^2(G-G')c^2}{\beta_1^4(\beta_1^2+H^2)a^2}e^{-a^2\beta_1^2t'/c^2}, \qquad (49)$$

t' being the time reckoned from the inversion P. The value, δ, of t', at which the dotted line crosses the full line in the figure, gives the displacement of the temperature maximum and for this value the lag L is zero. Hence to determine δ we have the equation

$$G'\left(\frac{1}{8}+\frac{1}{2H}\right)+\frac{4H^2(G-G')}{\beta_1^4(\beta_1^2+H^2)}e^{-a^2\beta_1^2\delta/c^2}=0. \quad . \quad (50)$$

Now for cases in which the first term of the series gives the lag with sufficient accuracy the value of

$$4H^2\beta_1^{-2}(\beta^2\beta_1+H^2)^{-1}$$

is very nearly equal to unity. For example, we have the following values for the cylindrical bulbs considered, and the values of

$$6H^2\alpha_1^{-2}\{\alpha_1^2+H(H-1)\}$$

for the spherical bulbs considered in para. 4:—Mercury sphere, ·999; alcohol sphere, ·865 (3 terms given); Mercury cylinder, 1·000; alcohol cylinder, ·978.

If H is small we have very nearly $\beta_1=\sqrt{2H}$, and so we find from (50)

$$\delta=\frac{c^2}{2Ha^2}\log_e\left(\frac{G'-G}{G'}\right). \quad . \quad . \quad . \quad . \quad (51)$$

But when H is very small, the value of the steady lag after the inversion is passed is

$$L'=\frac{G'c^2}{2Ha^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

Hence

$$\delta=\frac{L'}{G'}\log_e\left(\frac{G'-G}{G'}\right). \quad . \quad . \quad . \quad . \quad (53)$$

Note that δ depends only on the ratio of G to G′, and not on the absolute values of the gradients. In fact the value of δ as given by (51) is

$$\delta=\frac{c\rho\sigma}{2h}\log_e\left(1-\frac{G}{G'}\right).$$

For the mercury cylinder considered in para. 4, we found H=·0667, and so (53) should apply. Calculation yields the same values for δ as were found in para. 4.

As a numerical example we may consider the Kew Recording Thermometer. To obtain the values of the temperature time gradients, a series of monthly mean, diurnal temperature readings (Kew Records) was examined. The maximum value of the gradient occurs in the mornings (March–Sept.) and is 2°·0 F. per hour, or in degrees centigrade and seconds, $G_1=·000306$. The mean gradient for an hour preceding or following the maximum was found to be ·25° F./hour or $G_2=·0000389$. The surface conductivity is really given by a relation of the form

$$h=h_0+·0000515\,V,$$

where the constant term h_0 is negligible for aeroplane speeds, so that equation (30) then holds. In general, therefore, it will not be permissible to use (30) with small values of V. But as an example we shall take the cases in which

$V=2$ m.p.h. and $V=10$ m.p.h. The values of the lags and displacements obtained will then be upper limits.

The following data are given for the Kew Recording Thermometer (Mercury cylinder) :—

$K=\cdot 0197$, $a^2=\cdot 0437$.
$c=\cdot 425$ cm. = radius of bulb.
$l=10$ cm. = length of bulb.

CASE I. $V=2$ m.p.h. = velocity of air.
$h=\cdot 000103$ = surface conductivity.
$H=\cdot 002221$.

The formula for the steady lag becomes $L=933\,G$.

If $G=G_1=\cdot 000306$, $L=\cdot 29°$ C.
If $G=G_2=\cdot 0000389$, $L=\cdot 04°$ C.

These are, respectively, the greatest lag and the lag at the temperature maximum. The value of the displacement of the temperature maximum given by (53) is found to be

$$\delta=10^{\mathrm{m}}\,47^{\mathrm{s}}.$$

CASE II. $V=10$ m.p.h., $h=\cdot 000515$, $H=\cdot 01111$. The values of the lags and of δ are 1/5th those in Case I.

If $G=G_1$, $L=\cdot 06°$ C.
If $G=G_2$, $L=\cdot 01°$ C.
$\delta=2^{\mathrm{m}}\,9^{\mathrm{s}}$.

As previously stated, the true value of L and δ may be less than those given here, but they cannot exceed them.

8. *Cooling of Thermometers. Surface Conductivity and Orientation of Thermometer in Wind.*

The formula for the cooling of a thermometer bulb is much simplified when the first term of the series alone need be retained. In the case of a cylindrical bulb, we have for the mean temperature when the initial temperature (at $t=0$) has a constant value u_0, and the air temperature is zero everywhere, the effects of the ends of the cylinder being neglected :

$$\bar{u}=\sum_{n=1}^{\infty}\frac{4u_0H^2e^{-a^2\beta_n^2t/c^2}}{\beta_n^2(\beta_n^2+H^2)}, \quad . \quad . \quad . \quad . \quad . \quad (54)$$

where β_n is defined by equation (9). When the first term alone suffices we have approximately (see discussion of equation (50))

$$\bar{u} = u_0 e^{-a^2\beta_1^2 t/c^2} = u_0 e^{-2ht/c\rho\sigma}, \quad . \quad . \quad . \quad . \quad . \quad (55)$$

since $\beta_1 = \sqrt{2\mathrm{H}}$ when H is small.

For a spherical bulb, when the first term of the series suffices, the cooling equation, which is

$$\bar{u} = u_0 \sum_{n=1}^{\infty} \frac{6u_0 \mathrm{H}^2 e^{-a^2\alpha_n^2 t/c^2}}{\alpha_n^2\{\alpha_n^2 + \mathrm{H}(\mathrm{H}-1)\}}, \quad . \quad . \quad . \quad . \quad (56)$$

becomes

$$\bar{u} = u_0 e^{-a^2\alpha_1^2 t/c^2} = u_0 e^{-3ht/c\rho\sigma}, \quad . \quad . \quad . \quad . \quad . \quad (57)$$

since $\alpha_1 = \sqrt{3\mathrm{H}}$ when H is small.

Now the reading of a thermometer whose temperature is changing depends upon the mean value of the surface conductivity, h, over its surface. If the mean value of h varies when the thermometer is oriented differently in the wind, the mean temperature must also vary in consequence. Let us consider only metallic thermometers. For these, if $\mathrm{H} = ch/\mathrm{K}$ is small, we have for the cooling of the thermometer from a uniform initial value u_0:

$$\bar{u} = u_0 e^{-\lambda t}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (58)$$

$\bar{u}$ being the mean temperature; and λ is proportional to the surface conductivity, h, and is otherwise constant for a given thermometer. The time, T, required for the mean temperature to drop from u_0 to u_0/p is given by

$$\mathrm{T} = 1/\lambda \,.\, \log_e p. \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

When comparing the cooling of a thermometer in two orientations in the wind, for a given value of T, the values of λ are proportional to the corresponding values of $\log_e p$, *i. e.* for the same time of cooling,

$$\frac{h_1}{h_2} = \frac{\log_e p_1}{\log_e p_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

where the suffixes refer to the two orientations in the wind.

The following experiment was carried out to determine the ratio h_1/h_2 for the Short & Mason bimetallic thermometer described in para. 6. The strip in this case was ·5 cm. wide and made $4\frac{1}{4}$ turns with an outer radius of 3·0 cm. The gap between successive turns of the spiral varied from ·05 to ·10 cm. The surface was silver-plated to prevent rust.

This thermometer was mounted by itself on the top of a wooden block, the centre being 5 cm. above the top and near the edge of the block. An aluminium pointer 19 cm. long was fitted, and a scale, marked off in degrees, was mounted on the side of the block under the pointer. The scale could easily be read to ·1 division (·3° C.). The thermometer was heated in the dry inner vessel of a copper calorimeter, heated water being in the outer vessel and the block resting on the rim. When the temperature of the spiral was about 81° C. (room temperature 17° C.) the block was quickly removed, and the thermometer placed on the axis of a 30 cm. fan at a distance of 120 cm. from it. The air velocity at this distance, measured by manometer, was from 5 to 10 m.p.h. Times measured from the instant of removal and positions of the pointer were simultaneously recorded. In the first orientation the spiral cylinder was broadside to the fan draught. In the second it was end-on. In the latter position, about half the opening at each end was blocked by standards supporting the axis of the spiral cylinder, but there was a clearance between these and the spiral of at least 0·6 cm. The following table gives the data obtained, t being the time, $1/p_1$ the fractional drop in the "broadside" position, and $1/p_2$ the same in the "end-on" position. The values of p_1 and p_2 are means from two experiments in each position. Experiments in the same position showed good agreement.

t.	p_1.	p_2.	$\log_e p_1/\log_e p_2$.
0^s	1·00	1·00	—
15	1·73	1·54	1·27
30	2·92	2·38	1·24
45	5·29	3·58	1·31
60	8·46	5·18	1·30
90	20·9	10·02	1·32
120	49·1	16·2	1·40
150	80	23·2	1·39
180	113	35·4	1·32
210	200	55	1·32
240	310	75·2	1·33
270	620	93	1·42
		Mean.........	1·34

Hence $h_1/h_2 = 1{\cdot}34$, that is, turning the thermometer from "end-on" to "broadside-on" increases the surface conductivity by 34 per cent.

The thanks of the author are due to Mr. Gold for suggesting some of the problems, and to Mr. G. M. B. Dobson for many valuable suggestions and kind cooperation in numerous ways.

Royal Aircraft Establishment,
Farnborough,
Sept. 1919.

V. *Kinetic Stability.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

ALTHOUGH the idea of Kinetic Stability appears to be of considerable importance in certain Dynamical investigations, yet there are misunderstandings to be found in even some of the best text-books; and at the moment I am aware of only one book [*] which contains a good account of the theory accompanied by two or three well-chosen examples.

Still I should hardly have troubled you with these remarks, if I had not chanced to come across a very misleading statement on the subject of Kinetic Stability in Mr. Jeans's recent Adams Prize Essay [†]. On account of the author's reputation, and of his very attractive presentation of the subject-matter, it seems likely that this Essay will soon be one of the standard sources of information on cosmical mechanics. It therefore seems desirable to warn readers against the oversight, so that they may not be misled in similar investigations.

The passage in question will be found in Art. 27 [‡]. Summing it up into a brief statement, it implies that when a dynamical system is referred to axes rotating uniformly, an instability is introduced; but this is plainly absurd, for if we make the change of variables

$$X = x \cos \omega t - y \sin \omega t, \quad Y = x \sin \omega t + y \cos \omega t,$$

where $x = \Sigma A_r \sin (\sigma_r t + \alpha_r), \quad y = \Sigma B_r \sin (\sigma_r t + \beta_r),$

then the new variables will remain as simple harmonic

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[*] Lamb's 'Higher Mechanics,' (See Ch. xi. Arts. 98, 99).

[†] 'Problems in Cosmogony and Stellar Dynamics.' Cambridge.

[‡] See the foot of p. 29 and the first half of p. 30.

functions of the time; although of course any single term in σt will be replaced by a pair of terms containing $(\sigma+\omega)t$ and $(\sigma-\omega)t$.

What appears to have been overlooked by Mr. Jeans is that these systems are not rendered unstable until frictional terms are introduced, the amount of the friction being proportional to the *relative* velocity; the facts are clearly brought out in two examples given by Lamb *.

A similar oversight appears to occur in the associated gyrostatic problem (of constant angular momentum) mentioned in Art. 29: incidentally, the equations there used are attributed to Schwarzschild (quoting papers dated 1896 and 1897). They appear to me to be simply a special example of Routh's general process † for ignoration of coordinates, published in his Adams Prize Essay of 1877.

But before leaving the topic of stability, it may be worth while to refer to the fact that errors have been made by attempting to infer instability from the method of small oscillations. The classical instance is the top, sleeping upright with such a spin as to satisfy *exactly* the critical condition of stability; then (using the method of small oscillations), Routh deduced that this top would be really unstable (Adams Prize Essay). About twenty years later Klein proved in his Princeton lectures that this top is really stable ‡.

It does not appear to be possible to give any complete test to settle the question of stability in these critical cases; but a number of general considerations are given in a paper of my own on this topic §, together with a detailed examination of the allied problem of a solid moving through liquid, accompanied by circulation round the solid; in this problem the critical cases may be either stable or unstable, according to a rather elaborate additional criterion.

It may be useful here to quote from Klein's paper, in reference to the general question of trying to discuss problems of stability by means of the method of small oscillations:—

"From the start this method of small oscillations lies open to severe criticism. In the so-called unstable case it is directly self-contradictory, since the quantities, which in the

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* Proc. Roy. Soc. (A) vol. lxxx. p. 168 (1908); or 'Higher Mechanics,' Art. 99, exs. 2, 3.

† See, for instance, Lamb's 'Higher Mechanics,' Art. 83.

‡ Bulletin of the American Mathematical Society, vol. iii. p. 129 (1897).

§ Proc. Lond. Math. Soc. (1) vol. xxxiii. p. 331 (1902).

construction of the differential equations are assumed to be *small*, become, after its integration, *large*. There is no reason whatever, therefore, for regarding the results as an approximation to the actual conditions. Even in the stable case the method lacks an accurate basis."

However, these remarks seem to me to be unduly severe, after having borne them in mind for the past twenty-four years. After a careful examination of a large number of special problems, I have never found the method lead to erroneous results, except in these critical cases (such as the top-problem settled by Klein); and it must be remembered that (even in the problems of Statics) the critical cases are inevitably associated with the examination of terms of higher order than is usually necessary.

I am, Gentlemen,
Your obedient servant,
T. J. I'A. BROMWICH.

St. John's College, Cambridge,
4 August, 1921.

VI. *On the Beating Tones of Overblown Organ Pipes.*
By V. LOUGH, *B.Sc., A.R.C.Sc.*[*]

[Plate I.]

1. *Introduction.*

ONE of the most interesting problems in Acoustics, on which much has been written without arriving at a complete solution, is the mechanism of the excitation of "flue" or "flute" pipes by blowing. According to Helmholtz, this is a simple matter of the wafting from side to side of the blade-shaped air-jet into and out of the mouth of the pipe under the influence of the oscillating motion of the air within the pipe itself. In his book on 'The Sensations of Tone' he explains how the air-jet maintains these oscillations; he suggests that, having no appreciable stiffness, the jet follows the inward motion of the air inside the pipe, and so delivers a puff of air at or just after the period of maximum condensation. From the discontinuous nature of these impulses he deduces that the forced vibrations maintained by them should, in the case of narrow pipes having free periods in nearly harmonic relation, produce a tone rich in upper partials, similar to that of stringed instruments: a deduction which is fully supported by experience.

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[*] Communicated by Prof. C. V. Raman, M.A.

The action of the jet, however, is in reality not such a simple matter as would appear from the above suggestion. Helmholtz's theory fails to account for the initiation of the vibration, for the well-known rise of pitch with wind pressure, quantitative determinations of which have been made by Blaikley, Rayleigh, and others, and also for the jumping of the pitch to a higher frequency which results from overblowing.

A summary of subsequent work on the subject, with full references, may be found in Winkelmann's *Handbuch* *. Attention may be drawn especially to the investigations of Hensen †, Wachsmuth ‡, and others on the behaviour of the air-jet, its breaking up into vortices, and the relation of the tones of the pipe to the so-called "edge-tones" resulting from the wind-rush against a wedge-shaped obstacle. Reference should also be made to a more recent paper by A. C. Lunn §, who has suggested that the rise of pitch with wind-pressure may be due to the kinetic stiffness or quasi-elasticity of the air-jet, and adduces measurements in support of his theory.

The character of the vibrations of the air in organ pipes and the influence on it of the wind-pressure have been studied experimentally by Raps ||. The photographic records which he obtained by an interference method show that the vibration which at low pressures is comparatively simple and consists mainly of the fundamental, develops overtones as the pressure rises, the octave becoming more and more pronounced as the fundamental diminishes and finally disappears. In certain cases he noticed a peculiar "rolling" tone produced at an intermediate stage, but did not pursue his investigations in this direction.

Now in its practical application for musical purposes, the organ pipe has been developed exclusively as an instrument for producing a steady tone, and any other condition, such as the "rolling" or wavy tones noticed by Raps, is carefully avoided in voicing, and previous investigations have been conducted on the usual steady tones. But these wavy tones so carefully avoided in practice are nevertheless interesting from a theoretical aspect, as suggesting a departure from the harmonic overtone relation in forced vibrations and a comparison with the more familiar wolf-note phenomenon in stringed instruments. In view of the

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* 2nd ed. vol. ii. pp. 435–446.

† *Ann. der Phys.* vol. xxi. p. 786 (1906).

‡ *Ibid.* vol. xiv. p. 467 (1904).

§ Physical Review, May 1920, p. 446.

|| *Ann. der Phys.* vol. l. p. 193 (1893).

importance of these wolf-notes in the theory of bowed instruments, as demonstrated by C. V. Raman [*] in his monograph on the subject, it was thought that an investigation of the corresponding phenomenon in organ pipes might lead to useful results.

2. *Experimental methods and Results.*

Having collected a number of wooden pipes of the ordinary open-ended type, each pipe was tested separately at various wind-pressures, and it was found that instead of jumping suddenly to the octave as generally supposed, in all or nearly all cases the transition is perfectly gradual and usually includes an intermediate stage extending over a considerable range of pressure in which regular beats occur before settling down to the regular octave tone. In one particular instance, selected on account of the prominence of the beats, the pipe having a pitch of approximately 300 vibs. per sec. and being voiced for a pressure of about 6–8 cm. of water, perfectly regular beats of a frequency of 8–10 per sec. were audible over a range of about 11–15 cm. pressure. The frequency of the beats is nearly constant throughout this range. From the results of analysis by ear with the help of spherical resonators, it seems that the beating or variation of intensity takes place mainly in the first and second overtones, the fundamental remaining steady or nearly so throughout its gradual decrease. The character of the phenomena evidently depends on the voicing of the pipe, but the relation between them has not been established.

In order to verify and enlarge these observations, a series of photographic records of the vibrations was taken, each under similar conditions but at different pressures, and these records are reproduced on the accompanying Plate. The eight upper curves are records taken with the particular pipe above referred to; the lowest one is a single record for another pipe selected at random.

These records were taken by means of the special phonodeik devised by Dr. P. H. Edwards and described by Prof. Raman in a recent paper [†].

In view of the unavoidable effect of the horn and membrane of the phonodeik and no doubt also of the acoustic properties of the room in tending to distort the form of the record obtained with the instrument, the

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[*] Bulletin No. 15, Indian Association for the Cultivation of Science, Calcutta (1918).

[†] Phil. Mag. Jan. 1920, p. 145.

Summary of Analysis of Wave-forms for Beating Pipe.

Wave.	Pressure.	Fundamental.	First Overtone.	Second Overtone.	Ear (aided by appropriate resonators).
1	10 cm.	·93	·11	·03	Overtones feeble; all steady.
2	11	·75	·06	·02	Overtones stronger; still steady.
3 *a*	12	·73	·12	·01	Beats audible in first and second overtones.
b	......	·83	·22	·02	
c	......	·94	·26	·02	
d	......	·76	·16	·02	
4 *a*	13	·78	·50	·06	
b	......	·66	·46	·05	
c	......	·66	·46	·04	
d	......	·61	·46	·04	Fundamental (?) and overtones all beating, but especially the second and third.
5 *a*	13·8	·52	·53	·05	Fundamental steady and reduced, octave beating strongly, twelfth less strongly.
b	......	·41	·52	·04	
c	......	·35	·53	·03	
d	......	·46	·51	·04	
6 *a*	14·5	·12	·47	·02	Fundamental and octave steady, slight beats in twelfth.
b	......	·13	·56	·01	
c	......	·15	·56	·01	
d	......	·11	·44	·03	
7	15·5	·075	·4	·008	Fundamental and twelfth disappearing; octave steady.
8	17	·076	·4	·006	Steady octave.

results cannot be relied on quantitatively, but they show clearly enough the cyclical character of the variation and the changing proportions of the partial tones with alteration of pressure. The results of the harmonic analysis from measurements of selected waves on each of these curves are exhibited for comparison with the results of the corresponding ear-tests in the accompanying table.

It will be seen from the figures in this table that instead of increasing steadily and then falling abruptly as might be expected, the amplitude of the fundamental after rising to a maximum falls off gradually with increasing wind-pressure. If beats occur at all in this partial, which is doubtful, they occur only over a short range. The octave increases gradually and develops well-marked beats before settling down to the final steady tone, while the twelfth increases to a maximum and then falls off and disappears with the fundamental; the beats are most prominent in this partial.

3. *Discussion of the Results.*

Following on the analogy pointed out by Helmholtz between the form of the vibration of the air in narrow flue pipes and that of a violin string under the action of the bow, and in view of the comparison already suggested between the beating tones of overblown pipes and the similar effects obtained with bowed stringed instruments in certain cases, we should be led to seek an explanation of the beating tones in the departure of the free periods of vibration of the air-column from harmonic relation and a failure of the air-jet to supply sufficient energy for the continuous maintenance of all the possible modes of vibration. There are, however, certain difficulties in accepting this view in its entirety. It is true that the end corrections being not quite independent of wave-length have the effect of rendering the partials slightly inharmonic, and a similar effect may also arise from the elasticity of the walls of the pipe. But beyond this point the analogy does not seem to help us, for it is difficult to suppose that the air-jet which at normal pressure exhausts only a small fraction of its energy in sustaining the full tone of the pipe, can become less effective at higher pressures.

Again, though the records of the actual vibrations show a cyclical variation, they do not at any stage show the very strongly marked fluctuation amounting almost to periodic disappearance of the fundamental vibration which is characteristic of the records with bowed instruments obtained at the wolf-note pitch.

We are therefore forced to seek an explanation of the phenomenon in the special characteristics of the air-jet in relation to the natural frequencies of vibration of the air enclosed in the pipe. Unlike the bow, the air-jet has, as we have seen above, certain periodic tendencies of its own arising from the formation of vortices. It has been observed by Wachsmuth * that the excitation of the pipe cannot be maintained steadily unless the lip of the pipe is beyond the breaking-up stage of the jet, and then only when the pitch of the edge-tones approximates to that of the pipe. If so, we may suppose the initiation of the vibration in the pipe to be due to the deflexion of the jet by vortex reaction, its maintenance to the controlling of the deflexions by the combined effect of the pulsations of the air-column and of the vortices forcing each other into step.

Then, if by raising the wind-pressure the frequency of the vortex pulsations tends to rise and finally breaks out of step, leaving the pulsations of the air-column to control the deflexions of the air-jet, though weakened by the discordance, the quicker vortex pulsations might act independently to excite that mode of vibration of the air-column corresponding to its next higher free period, which would be nearly but not quite the octave. In this way we should have virtually two independent generators, each exciting a composite forced tone consisting of harmonic partials but slightly out of tune with each other. This state of affairs would continue until the rise of pressure brought the frequency of the vortex pulsations into approximate agreement with the octave pitch, when the pipe would again give a steady tone at the higher pitch. It may be noted that on the above assumption the frequency of the beats would approximate to the difference between the frequencies of the natural and the harmonic overtones, and would remain nearly constant during the whole range of pressure, as seems to be the case in practice. Direct observation of the behaviour of the air-jet may be expected to furnish a test of the correctness of the suggestions made above. It is proposed at an early opportunity to undertake the experimental work necessary for this purpose.

In conclusion, the author wishes to express his cordial thanks to Prof. C. V. Raman, in whose laboratory and at whose suggestion this investigation was carried out, for the facilities placed at his disposal.

University College of Science, Calcutta,
May 3rd, 1921.

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* *Loc. cit.*

VII. *The Probability of Spontaneous Crystallization of Supercooled Liquids.*

By C. N. HINSHELWOOD, *Fellow of Trinity College, Oxford, and* HAROLD HARTLEY, *Fellow of Balliol College, Oxford* [*].

IT is well known that a supercooled liquid, even in the absence of a crystal nucleus, usually crystallizes spontaneously if the temperature is lowered sufficiently. Ostwald put forward the view that there exists a definite line of demarcation between the "metastable" region of temperature, in which crystallization cannot take place in the absence of a crystal nucleus, and the "labile" region, in which spontaneous crystallization is possible. Failure to crystallize in the metastable region is attributed to the non-survival of the minute crystals which may be formed momentarily as the result of favourable molecular encounters. It can be shown thermodynamically, and has been verified experimentally by Pavlov [†], that the smaller the dimensions of a solid particle the lower is its melting-point. The first formed minute crystals, therefore, may possess a melting-point below the temperature of the liquid, even though this is some degrees supercooled with respect to a large plane crystal face, and hence they have but a transitory existence. If, however, the temperature of the liquid is lower than their melting-point they continue to grow, and crystallization spreads throughout the system. The dividing line between the regions of non-survival and of continued growth is the metastable limit.

The experiments of Miers and Isaac [‡], Hartley [§], and others showed that various substances and solutions, when cooled, crystallized at more or less definite temperatures—often about 10 degrees below the melting-point or saturation temperature. Miers [||] considered that this supported Ostwald's theory of a metastable limit, but de Coppet [¶] pointed out that the distinction between the metastable and labile conditions was arbitrary, and that the probability of a nucleus large enough to survive and grow varies continuously with the temperature. The metastable limit

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[*] Communicated by the Authors.

[†] Pavlov, J. Russ. Phys. Chem. Soc. xl. p. 1022 (1908).

[‡] Trans. Chem. Soc. lxxxix. p. 413 (1906); Proc. Roy. Soc. A. lxxix. p. 322 (1907).

[§] Trans. Chem. Soc. xciii. p. 825 (1908).

[||] *Loc. cit.*

[¶] *Ann. chim. phys.* x. p. 457 (1907).

merely represents a stage, in principle somewhat ill-defined, at which the probability of crystallization becomes very great. De Coppet found * that after the lapse of varying intervals of time, supercooled liquids crystallized within the region which the metastable limit was supposed to bound. The experiments just quoted, however, show that in practice the probability of crystallization must vary very rapidly in the neighbourhood of this point.

The object of the experiments to be described in this paper was to determine the mode of variation with temperature of the probability of crystallization, in the hope of throwing some light on the nature of the causes which lead to the formation of a crystal nucleus in a supercooled liquid. Tammann † has measured the way in which the linear velocity of crystallization varies with temperature, and also the number of nuclei formed in a mass frozen suddenly at different temperatures, but not the probability of crystallization—that is, the probability of the formation of a single nucleus from an initially homogeneous liquid.

It is clear that to obtain results of quantitative significance a statistical method must be adopted. A large number of similar tubes must be filled with equal volumes of the liquid under investigation, and the number counted whose contents have crystallized at the end of various intervals of time at a constant known temperature.

A number of organic substances were investigated—salol, phenol, p.-toluidine, diphenylamine, and o.-nitrophenol, as these melt at convenient temperatures.

The procedure was to fill about a hundred tubes, to seal them, and tie them to a board ; or in some experiments where very light and small tubes were employed they were sewn to a piece of nickel gauze. The contents were then melted by immersion in a bath of water at a known temperature above the melting-point, sufficient time being allowed to ensure that all crystalline nuclei dissolved. The tubes were then transferred to a thermostat, and the number of crystallizations observed from time to time. When one experiment was completed, those tubes in which crystallization had not taken place were induced to crystallize as far as possible by immersion in cold water. Then the whole set were melted up again and a fresh experiment begun.

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* *Loc. cit.*

† 'Krystallisieren und Schmelzen,' Leipzig, 1903, p. 131.

The catalytic nature of the process of nucleus formation.

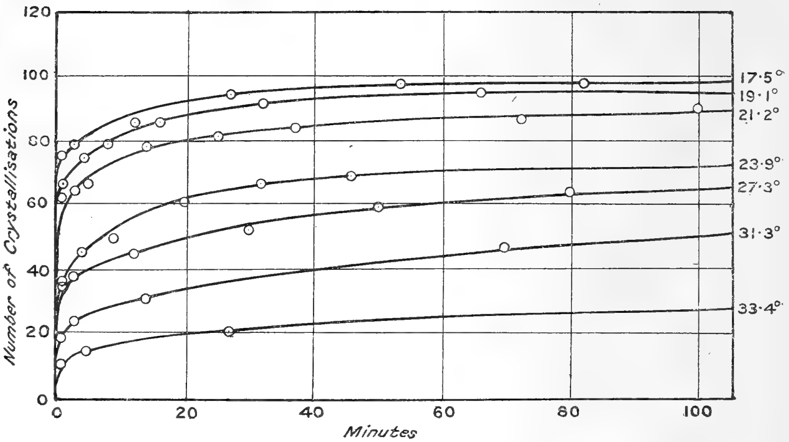
The study of the phenomenon is complicated from the outset by the fact that the formation of a nucleus is a catalytic process.

Previous observers have stated that the tendency of a supercooled liquid to crystallize depends upon the temperature to which it has been previously heated [*], on the number of times fusion and solidification have taken place [†], and on the length of time it has been maintained in the fused state [‡].

These influences were very evident in our first series of experiments, which were made with salol contained in steamed-out soda-glass tubes 5 cm. × 0·8 cm. Equal volumes (about 2 c.c.) of salol were placed in all the tubes, which were numbered so that an individual record of each might be kept. The results are given in Table I. (see p. 92).

With seventy tubes fairly smooth curves were obtained for the relation between time and number of crystallizations.

Fig. 1.—Spontaneous crystallization of Para-toluidine.



This justifies the application of the laws of probability to the results. The form of the curves is explained in the next section. (The salol results are not plotted here, but the similar series with p.-toluidine is shown in fig. 1.)

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[*] de Coppet (*loc. cit.*).

[†] Karl Schaum, *Zeitschr. phys. Chem.* xxv. p. 722 (1898).

[‡] *Ibid.*

De Coppet's statement that salol shows less tendency to crystallize the higher the temperature to which it has been heated is confirmed, and in addition a rough quantitative measure of this influence is obtained.

Maximum temperature to which the salol has been heated after sealing of tubes.	Relative probability of crystallization at 32°·3 C. (The method of calculating this number is explained in a later section.)
circa 60°	1000
circa 65°	570
75°	240
85°	72
100°	2

It must be emphasized that the diminution in the tendency to crystallize is governed by the highest temperature to which the salol has been previously heated, independently of whether it has been allowed to crystallize or not in the meantime. Thus, for example, after the tendency to crystallize had been decreased by heating at 80°, the contents of the tubes were made to solidify; they were then melted at 50°, when they behaved almost exactly as in the experiment immediately preceding, having regained none of their power of crystallizing. This is important, because it disposes of two possibilities: (1) that the diminished probability of crystallization after heating is merely due to the more complete removal of residual crystal nuclei, and (2) that it may be due to some change in the molecular state of the liquid brought about by the heating.

Although the most marked and rapid diminution in the tendency to crystallize is produced by heating, a slow "ageing" effect gradually becomes evident, even in a series of experiments in which the melting-up process is effected at a constant temperature. The tendency of some tubes to crystallize diminishes progressively.

Possible explanations of these facts are: (1) that gradual solution of alkali from the glass has a disturbing influence, (2) that gradual decomposition takes place, or (3) that some catalytic agency provoking crystallization gradually loses its activity.

That the last explanation is the correct one is shown conclusively by opening the tubes, exposing the salol to the air, and re-sealing. After a few days' exposure to the air in a cupboard the salol had regained its lost power of crystallizing, when the tubes were treated exactly as before.

It seems clear, therefore, that the fine organic dust particles which are always floating in the air (Tyndall) are effective agents in provoking crystallization. This conclusion is supported by the observation of Jaffé * that repeated and intensive filtration of a liquid reduces its power of crystallization. Crystallization of an organic liquid seems, therefore, to be analogous to the condensation of a supersaturated vapour.

Since these particles lose their activity as a result of heating, and also, but less markedly, as the result of ageing, they are probably colloidal in nature. The formation of a nucleus thus appears to be due to heterogeneous catalysis, the effect of heating and ageing being to change the degree of dispersion of the colloidal system, and hence its activity.

Similar behaviour after heating was also found with phenol (Table II.), p.-toluidine (Table III.), and diphenylamine.

The following results relating to the "temperature of spontaneous crystallization" illustrate the same point :—

p.-Toluidine heated in a tube for some time at 100° crystallized when cooled at 18°·5 and 17°·5. After opening and exposing to the air, re-sealing, and melting at 50°, crystallization took place on cooling at 28°·5 and 28°·5.

α-Naphthylamine in a tube heated to 100° crystallized on cooling at 14°·9, 13°·6, 16°·0, and 13°·3. After exposure to air, crystallization took place at 28°, 33°, and 29°.

The relation between Time and Number of Crystallizations.

Suppose there are n_0 tubes, and the number whose contents have crystallized after a time t be n; then the relation between n and t can give some information about the nature of the phenomenon of nucleus formation. If, for instance, a nucleus were formed as a result of slow consecutive changes in the solution, then $\frac{dn}{dt}$ would have a maximum at a certain point. There is, however, no sign of such a maximum.

If, on the other hand, the formation were the result of random chances, and the chance of formation were the same for each tube, then n and t would be connected by the same exponential relation as is found for a unimolecular chemical reaction $n=n_0(1-e^{-\chi t})$, where χ is a constant whose magnitude measures the probability of crystallization.

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* *Zeitschr. phys. Chem.* xliii. p. 565 (1903).

The experimental results show, however, that an abnormally large number of tubes tend to crystallize in the very early stages, and that the later stages are always drawn out much longer than the exponential relation given above allows (see curves in fig. 1). In other words, the tendency to crystallize is different in different tubes. For example, in the salol experiments tube 9 almost invariably crystallized very early while tube 18 was as frequently still unchanged at the conclusion of the experiment. As the phenomenon appears to be catalytic this is not surprising, as the amount and activity of the catalyst may vary from tube to tube.

In this case we might assume that the exponential expression held, but that χ instead of being constant had values distributed about a most probable value—*e.g.*, that the number of tubes for which χ lay within a certain range was given by some such distribution law as

$$dn_0 = a\chi^2 e^{-h^2\chi^2} d\chi,$$

so that

$$n_0 = \int_0^\infty a\chi^2 e^{-h^2\chi^2} d\chi.$$

Then

$$n = \int_0^\infty a\chi^2 e^{-h^2\chi^2}(1-e^{-\chi t})\, d\chi\,;$$

so that

$$n = n_0 - e^{t^2/4h^2}\left(\frac{a}{2h^2}+\frac{at^2}{4h^4}\right)\int_{t/2h^2}^{\infty} e^{-h^2x^2} dx + \frac{at}{4h^4}.$$

This gives a curve steeper initially than the monomolecular curve and reaching its limiting value more slowly.

The curves (*e. g.* those in fig. 1) cannot, however, be represented even by an expression like this with distributed values of χ, being far too steep in the first short interval of time.

Experiments were made with p.-toluidine, diphenylamine, and o.-nitrophenol in very thin small tubes, about 1 mm. by 20 mm., which very rapidly attained thermal equilibrium when plunged in the thermostat. The results obtained with these (Tables III. and IV.) show that at a given temperature a certain proportion of the tubes crystallize *almost instantaneously*, and that among the remainder there is a distribution of activities something like that suggested above.

The probable explanation seems to be as follows:—Nucleus formation occurs round the colloidal particles which the liquid has derived from the air. An adsorbed layer is presumably formed in which the molecules are orientated. If the radius of the particle is equal to or greater than that of the particles of solid which would be in equilibrium with the liquid at the temperature of the experiment, then the nucleus will grow and crystallization will take place immediately. But if the radius of the dust particle is smaller than this equilibrium radius, then crystallization will not take place until, as the result of a series of fortunate chances, the nucleus has been built up to the necessary size. The average time which must elapse before this happens obviously depends upon the discrepancy between the radii of the largest active dust particles present and the radius of the nucleus which is first capable of continued growth.

The Influence of Temperature.

The curve in fig. 1, which refers to p.-toluidine, and the numbers in Tables III. and IV. show that as the temperature is lowered, the number of crystallizations taking place almost instantaneously increases largely, but that the remainder of the curve resembles exactly some portion of a curve for a higher temperature.

The radius of the particles in equilibrium with the liquid diminishes with temperature. Hence, some of the dust particles too small to effect immediate crystallization at one temperature may be able to do so at a lower temperature. As the temperature falls the average life of each tube diminishes, and some reach a critical temperature at which crystallization takes place at once. This is in a sense a compromise between the views of Ostwald and de Coppet.

The dependence of average life upon size of particle present.

The attempt to determine this is rendered more difficult by the gradually changing degree of dispersion of the colloidal particles throughout a series of experiments.

Madinaveitia and Aguirréche [*] and Rocasolano [†] have shown that as a platinum sol ages and its degree of dispersion diminishes, its catalytic activity first increases slightly and then decreases. A precisely similar effect is found in the formation of crystal nuclei, but only rarely is there an initial increase. It is found that with diphenylamine the tendency to crystallize at first increases and then falls off—the increase being due probably to the initial

[*] *Anal. Fís. Quím.* xix. p. 124 (1921).
[†] *Anal. Fís. Quím.* xix. p. 114 (1921).

increase in the size of the colloidal particles present, and the decrease to the subsequent destruction of their activity owing to coagulation or some other cause. The loss of activity is the general rule, and may be so serious as to make one experiment incomparable quantitatively with the next. This was unfortunately the case with diphenylamine. o.-nitrophenol was more satisfactory, while a set of tubes filled with p.-toluidine was sufficiently "stable" for a whole series of experiments to be carried out under approximately constant internal conditions. The details of these are now given.

The procedure is as follows :—

(*a*) To calculate the variation with temperature of the radius of p.-toluidine particles in equilibrium with the liquid.

(*b*) To determine the number of tubes of p.-toluidine which crystallize instantaneously at a given temperature.

By combining (*a*) and (*b*), we find how many tubes contain active dust particles whose radius is greater than a certain value.

(*c*) From the n, t curves at different temperatures to find the average life of tubes containing particles of radius between certain limits.

(*a*) Ostwald [*] showed that this could be calculated from the surface energy of the solid. Jones and Partington [†] have made a similar calculation.

The following is a modification of Ostwald's calculation, introducing Nernst's Heat Theorem :—

Let A be the free energy of the process of crystallization of a supercooled liquid with respect to a plane surface of the solid. Then, by Nernst's Heat Theorem [‡],

$$A = U_0 - \beta T^2,$$

where U_0 and β have the conventional meanings.

Let r be the radius of small particles of the solid which would be in equilibrium with the liquid at the temperature T; then, if σ be the surface energy of the solid and ρ its density, the work done when one gram of the solid is changed from particles of radius r to radius ∞ (*i. e.* a plane surface) is $\frac{2\sigma}{\rho r}$.

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[*] *Zeitschr. phys. Chem.* xxxiv. p. 495 (1900).

[†] Phil. Mag. xxix. p. 35 (1915).

[‡] Nernst, Theor. Chem. 4th Eng. ed., p. 750.

This must be equal to A;

$$\therefore \quad J(U_0-\beta T^2)=\frac{2\sigma}{\rho r} \quad \text{or} \quad r=\frac{2\sigma}{\rho}\,\frac{1}{(U_0-\beta T^2)J}.$$

σ is not known precisely; but since for the small temperature differences of a few degrees with which we are concerned we may regard it as constant, the variation of r is chiefly governed by $\dfrac{1}{U_0-\beta T^2}$.

From the melting-point of p.-toluidine, 43°·3, and its latent heat of fusion, 39 cals. per gram, U_0 and β are calculated in the usual way; whence

$$r=\frac{2\sigma}{\rho}\,\frac{1}{(19{\cdot}5-{\cdot}000195T^2)J}\ \text{cm.},$$

where

$$J = \text{Mech. Equiv. of Heat.}$$

This allows us to calculate the following values of r, which are plotted against temperature in fig. 3:—

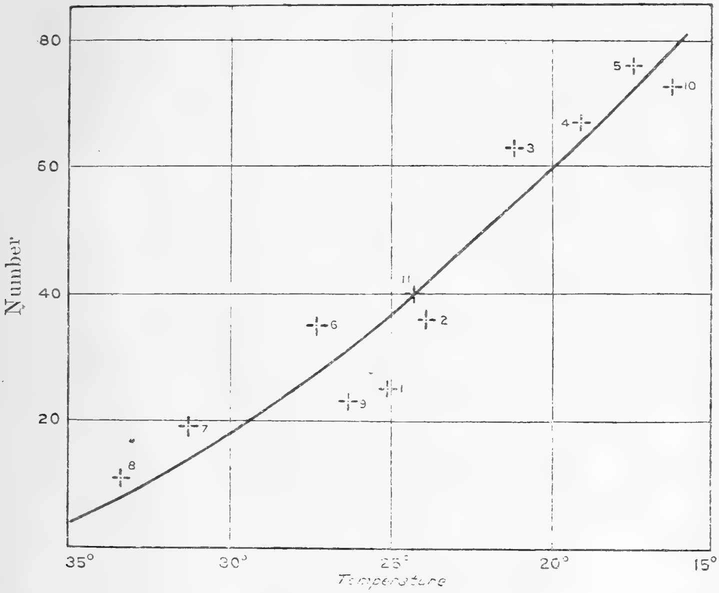
Variation with temperature of radius of particle in equilibrium with liquid.

Temp.	r.
35° C.	$0{\cdot}24\times10^{-7}\times\frac{2\sigma}{\rho}$ cm.
30	0·15
25	0·11
20	0·086
15	0·072

(*b*) Fig. 2 gives the number of tubes of para-toluidine out of the 122 used, which crystallized instantaneously at different temperatures. The points are numbered in the order in which the measurements were made, to illustrate the comparative absence of progressive changes in activity. We now suppose that those tubes in which crystallization occurred instantaneously contain active particles of radius equal to or greater than the equilibrium radius for this temperature, and thus by eliminating the temperature between curves 2 and 3 we obtain the distribution of particles of various radii among the tubes. Curve 4 gives the number of tubes containing active particles with radii greater than a certain limit.

Fig. 2.—Number of tubes of Para-toluidine crystallizing within one minute at various temperatures.

[The points are numbered in the order in which they were determined.]



(*c*) Now from the statistical n, t curves (fig. 1) we can proceed to find the average life of tubes containing particles not quite large enough to provoke immediate crystallization. The working out of an actual example will make the method of procedure clear.

Consider the curve referring to 122 tubes of p.-toluidine at 31°·25. The number crystallizing within the first minute is 19. On the smoothed curve (in fig. 2) 19 corresponds to a temperature of 29°·8, the difference being due to variations in the activity of colloidal matter from one experiment to another. We regard, therefore, 29°·8 as the corrected temperature. The equilibrium radius at this temperature is 0·147 × constant. We can now estimate the average life of tubes containing particles within 20 per cent. of this size—*i. e.*, between 0·147 and 0·118. Fig. 4 shows that there are 32 tubes with particles greater than 0·118—that is, $32-19=13$ tubes with particles whose radius is not more than 20 per cent. less than that of the particles provoking immediate crystallization. From the n, t curves (fig. 1) we

Fig. 3.—Para-toluidine.
Variation of equilibrium radius with temperature.

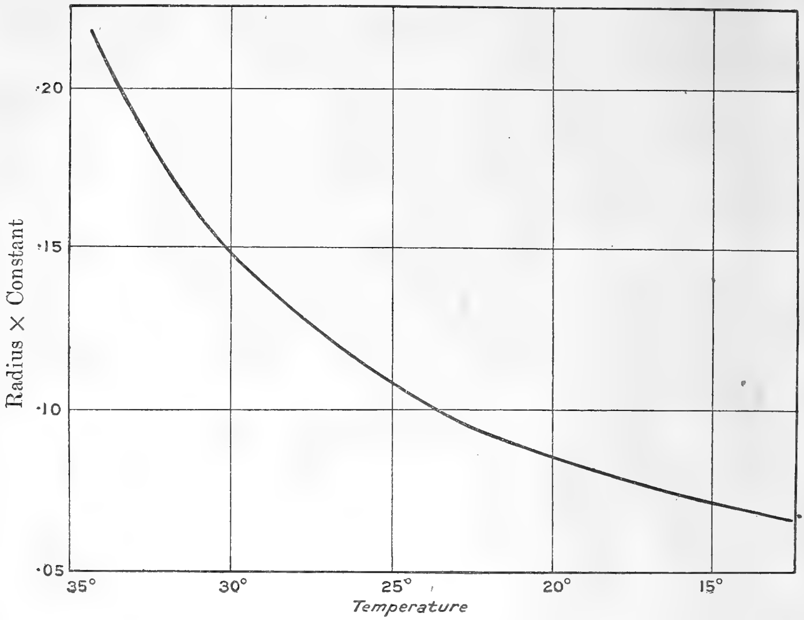
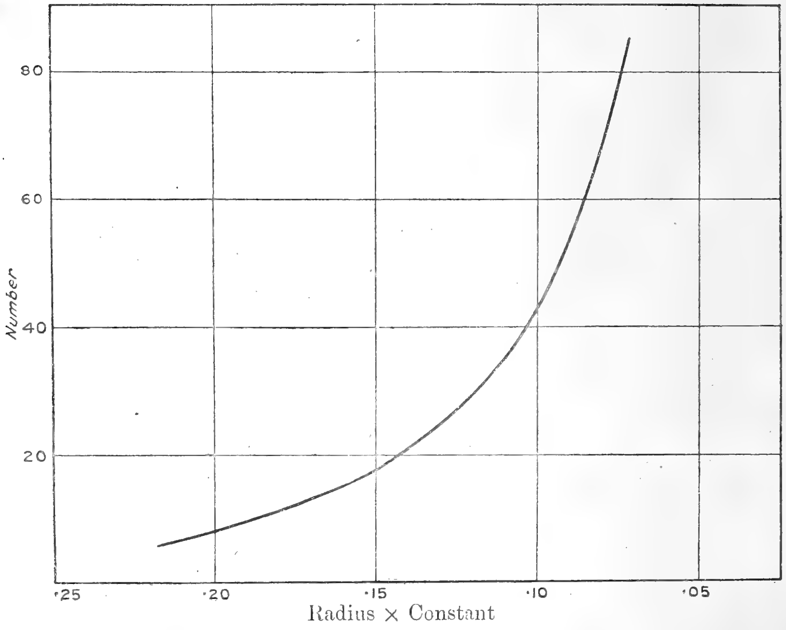


Fig. 4.—Para-toluidine.
Number of tubes containing particles of radius greater than a given value.



see that 17 minutes were required for the number of crystallizations to increase from 19 to 32—that is, the average life is in this case about 8 minutes [*].

Similar calculations yield a fairly consistent picture for the whole series of experiments; thus:—

Temperature of experiment.	Average life, in minutes, of tubes containing particles whose radius differs from the equilibrium size by 0–10 p. c.	10–20 p. c.	20–30 p. c.	30–40 p. c.
33°·4	3	13	75	360 approx.
31°·3	2	10	32	290 approx.
23°·9	2	9	52	670 approx.
19°·1	4	80 approx.		

It is evident, therefore, that as the discrepancy between the radius of the particle of equilibrium size and the radius of the particle present increases by equal fractions, the average life increases more or less geometrically.

As we have said, the tubes of diphenylamine were of variable activity and showed an initial increase. Although their behaviour was in accordance with the theory suggested, it made a series of comparative measurements difficult. Exactly the same general relations however appear, as is shown by the following numbers, which refer to an experiment at 34°·0 with 133 tubes:—

Time, in minutes.	Number of crystallizations.
1	34
4	39
16	47
55	49
80	54
95	56
1340	63

The calculations of particle size, etc., are not given, but lead for the above experiment to the following result:—

	Discrepancy between equilibrium size and size of particle present. 0–10 per cent.	10–20 per cent.	20–30 per cent.
Average life, in minutes ...	6 approx.	50 approx.	> 700

i. e., the same sort of relation as previously found with p.-toluidine.

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[*] The justification for calculating the average life in this simplified way is the rapidity with which the number of crystallizations in successive intervals of time falls off.

o.-Nitrophenol was found to behave in a similar manner, both as to the form of the curves showing the relation between number of crystallizations and time, and as to the average life relationships. There was, however, a considerable variability in the tendency to crystallize from experiment to experiment and in the distribution of sizes, such as to hinder accurate calculation.

An experiment at 38°·7, the first of the series carried out (see Table IV.), gave the following approximate results :--

	Discrepancy between equilibrium size and size of particle present.			
	0–10 p. c.	10–20 p. c.	20–30 p. c.	30–40 p. c.
Average life, in minutes ...	5	30	115	290

Effect of Heating on the form of the crystallization-time curves for a given set of tubes.

The effect of heating in causing a general diminution in the tendency to crystallize has already been dealt with. But the effect of heating for a given period at a given temperature does not necessarily influence the activity of all the tubes to the same extent. For example, the most active tubes may at first be sterilized most rapidly, so that the curves change somewhat in form. This may be seen from one of the experiments on p.-toluidine.

If it were possible to bring all the tubes into exactly the same state, the curve would become a unimolecular curve ; and it was by applying a unimolecular formula as an approximation to a portion of the salol curves that the relative values for the tendency to crystallize (p. 81) were calculated.

Discussion.

To estimate the actual size of the particles about which crystallization takes place it is necessary to know the value of the surface energy of the solid. Little information is available about the numerical magnitude of this property, but the experiments of Hulett on the dependence of the solubility of certain sparingly soluble salts on the size of particles indicates that it is the neighbourhood of 10^3 (*cf.* Partington and Jones, *loc. cit.*), and numbers of the same order may be deduced from the experiments of Pavlov on salol.

In these series of experiments (p.-toluidine, diphenylamine, and ortho-nitrophenol) the contents of half of the tubes crystallized instantaneously at temperatures where the equilibrium radius was of the order $0{\cdot}1$ to $0{\cdot}2 \times 10^{-7} \times \frac{2\sigma}{\rho}$.

Taking ρ as 1 to 2, and σ as 10^3, this gives a value for r of the order of 2×10^{-5} cm., which is equivalent to about three hundred molecular diameters.

Consisting of a foreign substance which does not dissolve, the particle acts as a centre upon which successive layers of molecules may be deposited. If it is 30 per cent. too small to bring about immediate crystallization, successive layers are deposited, but continually re-dissolve until by chance a succession of depositions carry it past the critical size. This appears to happen after an average life of about an hour in the case of p.-toluidine, where this 30 per cent. increment seems to represent about 100 layers of molecules.

Theoretically a particle of sufficient size should relieve supercooling, even in quite close proximity to the melting-point, but a limit is set by the well-known fact that colloidal particles become less active when their size increases beyond a certain value. The reason for this is not clearly understood, but the magnitude of this limit is probably as specific as all other catalytic phenomena.

It would be rash to assume that the relationships described in this paper are entirely general, but a well-defined class of cases seem to come within the scope of the principles suggested.

We hope to carry investigations further by ultra-microscopic observation, as this seems to be the direction in which results of some interest in connexion with the problems of surface energy might be found.

Summary.

The statistical investigation of the spontaneous crystallization of several supercooled organic liquids leads to the following conclusions :—

1. In the case of these substances crystallization is provoked by the colloidal organic dust particles from the air.

2. The activity of these particles diminishes in general as the result of heating or ageing.

3. Their effectiveness depends upon their radius. If this is equal to the radius of a small particle of the solid which should thermodynamically be in equilibrium with the supercooled liquid, then crystallization occurs at once. If the radius is less than this, the supercooled liquid has an average life depending on the discrepancy between the equilibrium radius and the radius of the particles present.

The magnitudes of these quantities are discussed.

TABLE I.

Salol. 70 tubes. 16 experiments were made, of which the following are typical. The experiments are numbered in the order in which they were carried out:—

M.P. of Salol = 42°·5.

1. Melted at 60°. Temp. of thermostat 32°·3.

Time in hours.	Number of crystallizations.
0·1	21
0·2	29
0·3	32
0·5	35
1·3	40
5·0	35
8·0	37
23	62

2. Melted at about 65°. Temp. of thermostat, 32°·3.

Time in hours.	Number of crystallizations.
0·1	26
0·3	34
0·5	36
2·5	37
7·8	44
10·5	46
23	55
33	61

3 Melted at 75°, allowed most to crystallize, and melted again at 57°. Thermostat, 32°·3.

Time in hours.	Number of crystallizations.
0·5	19
2·5	29
15	38
22	42
39	48

4. Heated to 85°. Temp. of thermostat, 32°·3.

Time in hours.	Number of crystallizations.
0·5	12
2·0	24
15	30
47	34
72	39
136	45
158	50
208	55
279	59

5. All tubes except one made to crystallize. Then melted at 49°–50°. Temp. of thermostat, 32°·3.

Time in hours.	Number of crystallizations.
0·5	16
1·0	19
5	29
19	30
43	34
67	40
100	44
140	49
165	50
212	52
236	55
260	57

6. Melted again at 50°. Thermostat, 36°·5.

Time in hours.	Number of crystallizations.
5	18
21	24
125	27
216	29
305	33
453	35

7. Melted at 50°. Thermostat, 20°·5.

Time in hours.	Number of crystallizations.
2	36
26	45
150	48
300	51

8. Heated the whole batch of tubes to 95°–100° for 5 hours. In thermostat at 32°.

[*Cf.* experiments 1–5.]

Time in hours.	Number of crystallizations.
48	13
216	18
792	24
1050	24

9. Tubes opened and exposed to the air in a cupboard for 4 days. Re-sealed 36 tubes. Melted at 50°. Temp. of thermostat, 35°.

Time in hours.	Number of crystallizations calc. for 70 tubes (*i. e.* actual number × 70/36).
0·5	19
8	35
23	39
70	49

10. Melted at 50°. Temp. of thermostat, 28°·8.

Time in hours.	Number of crystallizations calc. for 70 tubes.
6	56
20	63

TABLE II.

Phenol. 41 tubes. (12 expts. made.) The following are typical :—

1. Melted at 50°.
Temp. of thermostat, 18°·0.

Time in minutes.	Number of crystallizations.
10	3
25	14
40	20
230	32
1200	38

2. Melted at 50°.
None crystallized in 15 days at 25°.

3. Melted at 50°.
Temp. of thermostat, 20°·0.

Time in minutes.	Number of crystallizations.
30	10
900	26
2300	29

4. Tubes heated at 100° for 2 hours.
Temp. of thermostat, 18°·0.

Time in minutes.	Number of crystallizations.
10	3
200	12
1400	17

TABLE III.

Para-toluidine. 122 tubes, sufficiently small to attain the temperature of the bath very rapidly.

Melted at 50° in each case.

t = time in minutes; n = number of crystallizations.

1. *23°·87.*		**2.** *21·°18.*		**3.** *19°·12.*		**4.** *17·°48.*	
t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
1	36	1	63	1	67	1	76
4	46	3	65	4	75	3	79
8	50	5	67	8	79	12	86
20	62	14	79	16	86	27	95
32	68	25	82	32	92	53	98
46	70	37	85	66	96	95	100
54	71	72	88	82	99	285	104
345	84	100	92	150	100	1000	114
1320	96	530	101	180	101		
				300	103		

5. *27°·32.*		**6.** *31°25.*		**7.** *33°·36.*		**8.** After heating to 100°. *24°·8.*	
t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
1	35	1	19	1	11	1	15
3	38	3	24	5	15	5	20
12	45	14	31	27	21	16	26
30	53	70	48	115	27	30	37
50	60	120	51	215	34	210	62
80	65	210	53	345	37	1020	84
115	68	370	56	1380	41	1365	87
395	75	1345	62			2490	93
1350	80						

TABLE IV.

Ortho-nitrophenol. 130 tubes.

Tubes once heated to 70°, contents allowed to solidify, and then re-melted at 50° in each case.

t = time in minutes; n = number of crystallizations.

1. *38°·72.*		**2.** *34°·25.*		**3.** *36°·07.*		**4.** *33°·52.*		**5.** *31°·1.*	
t.	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*	*t.*	*n.*
1	21	1	60	1	27	1	58	1	57
3	24	3	69	3	28	3	64	4	66
15	33	15	91	15	35	10	72	17	79
30	39	45	99	48	50	22	82	47	101
45	42	90	106	168	72	45	94	90	107
75	46			270	80	70	101	285	112
115	49			375	89	130	108		
240	58			1420	105	310	112		
315	60								
630	67								
1350	70								

Numbers of tubes crystallizing within 1 minute at various temperatures:—26°·2, 126; 28°·9, 113; 31°·6, 80; 34°·25, 86; 35°·95, 67; 37°·7, 62; 39°·85, 40; 42°·0, 0; 40°·0, 19; 37°·9, 48; 35°·8, 54; 34°·0, 62; 32°·6, 63; 29°·5, 66; 26°·0, 119.

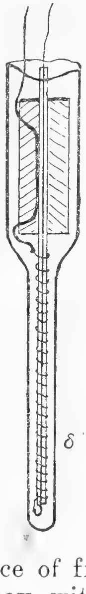
VIII. *On the Insulation of Highly Attenuated Wires in Platinum Resistance Thermometers.* By J. J. MANLEY, *M.A., Research Fellow, Magdalen College, Oxford* *.

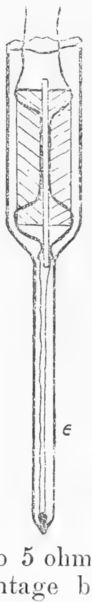
THE construction of platinum thermometers having bulbs with a diameter of 2 mm. and resistance wires the thinness of which ranges from ·06 to ·02 mm., presents some difficulties of an exceptional order. Of these the greatest is probably that encountered when we proceed to support and insulate the highly attenuated wire. The cross frame of mica introduced by Griffiths, being from lack of space inadmissible, the difficulty can only be surmounted by having recourse to other methods. By trial it was ultimately found that in addition to the plan first described by Burstall † and subsequently by Callendar and Nicholson ‡ three others were available: these we now briefly describe.


α


β


γ


δ


ε

1. In all cases where a resistance of from 3 to 5 ohms suffices, Burstall's simple plan may with advantage be followed, the wire being arranged as a loop as shown in fig. α. Placed *in situ*, much of the loop makes contact with the containing tube: this is helpful, for the thermometer is thereby enabled all the more readily to acquire the temperature of the surrounding medium. If the loop is well

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* Communicated by the Author.

† Phil. Mag. Oct. 1895.

‡ Proc. Inst. C. E. 1893.

formed and carefully arranged within its tube, short-circuiting becomes impossible.

2. When for a given purpose a short wire offers too small a resistance, Burstall's plan becomes for highly attenuated wires, imperfect ; this is due to the absence of the necessary stiffness in the wire. The defect is successfully met by inserting a thin slip of mica between the two limbs of the loop, as shown in fig. β. The upper end of the slip is held between the two stouter pieces of mica to which are fastened the thermometer leads, and the other end is notched for the reception and retention of the lowest part of the loop. As an alternative the slip may be pierced with a needle near the lower end, the resistance wire being then threaded through the hole, drawn taut, and finally fused to the leads. Loops of any desired length may be mounted and highly insulated in this way.

3. For a thermometer having a high resistance, the supporting insulator consists of two plates of mica each about 1 mm. thick, and cut as shown in fig. γ. The wide and shorter portions of the plates are held between two others which are used for supporting the platinum, gold, or silver leads, and all four firmly bound together with fine nickel wire. One lead is made to terminate just below the compound block ; but the second lead is longer and its lower portion is hammered flat and placed between the two narrow limbs of the central slips of mica, with its end slightly projecting. The resistance wire having been fused to the longest lead, is wound spiral-wise, as shown in fig. δ, upon twin slips, and finally fused to the second and shorter lead. It is then ready to be introduced into its protecting tube.

4. More recently we have adopted the following convenient and very efficient plan for insulating and supporting highly attenuated wire loops of any required length. A glass rod about 1 or 2 mm. in diameter is prepared and a needle-eye formed at one end. Having fused one end of the resistance wire to the lead, the other end is drawn through the eye in the glass rod and brought up and secured to its lead. Holding the leads vertically, the rod will, if of appropriate weight, pull and maintain the loop taut. The wires are now placed within their protecting glass tube, the lower end of which is open and of such dimensions that the rod suspended from the resistance wire can just pass through. Still keeping the thermometer vertical, and applying a suitable blowpipe-flame, the lower end of the tube is closed by fusing it to the glass rod. When cold, the superfluous glass is cut off and the end rounded in the flame. Fig. ϵ shows a completed thermometer-bulb of this form.

Daubeny Laboratory,
Oxford.

IX. *The Equations of Equilibrium of an Elastic Plate under Normal Pressure.* *By* JOHN PRESCOTT, *M.A.*, *D.Sc.*, *Lecturer in Mathematics in the Faculty of Technology of Manchester University* *.

THE earliest writers who had any success with the problem of the bending of an elastic plate followed the analogy of the beam so faithfully that they missed altogether one very important difference between a plate and a beam or rod. They were so obsessed with the idea that only the curvatures of the plate mattered that they ignored the effect of the stretching of the middle surface that must accompany any bending of the surface. It is a very well-known fact that a plane area cannot be made to fit on the surface of a sphere, for example, without a stretching or contraction of some of its parts. Yet this strain has nearly always been neglected by writers on the bending of thin plates. It is true that there are many cases in which it is justifiable to neglect these stretchings and shortenings, but there are so many practical problems in which it is not justifiable that no theory of thin plates is satisfactory which does not take them into account, or else point out the limitations of the restricted theory.

The usual Poisson-Kirchhoff equations need no alteration when the maximum deflexion of any particle of the middle surface is small in comparison with the thickness of the plate, this deflexion being measured from a plane which touches the middle surface at any convenient point, or from any developable surface which touches the middle surface at any point and nearly coincides with it elsewhere. But when this deflexion is of the same order as the thickness, then Poisson's equations may be very much in error. In such cases the mean tensions over sections perpendicular to the middle surface play as great a part in supporting a pressure on the plate as do those stresses of which the usual theory takes account. In fact, to make Poisson's theory correct there must be quantities of three different orders of magnitude. In ascending order these quantities are

(1) the maximum deflexion perpendicular to the unstrained middle surface or perpendicular to a developable surface;
(2) the thickness of the plate;
(3) the lateral dimensions of the plate.

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* Communicated by the Author.

The only previous reference to this limitation that I am aware of occurs in Thomson and Tait's 'Natural Philosophy.' They state (Art. 632) that "the deflexion is nowhere, within finite distance of the point of reference, more than an infinitely small fraction of the thickness." They had already worked out (Art. 629) the mean circumferential strain of a small circular portion of the middle surface of a plate which is bent into a surface with principal curvatures ρ_1 and ρ_2 when the radial lines are unstrained. From their result they justify the limitation that they impose.

The footnote added to the above quotation from Thomson and Tait by Professor Karl Pearson in the 'History of the Theory of Elasticity' shows how little the point was understood. The footnote runs thus: "The pressure of the finger on the bottom of a round tin canister seems to produce a deflexion which is far from being an infinitely small fraction of the thickness, and which might, I think, be fairly discussed by the ordinary theory." I regard this footnote, written by the author of such a complete history of the modern developments of the subject, as very good evidence that no other writers have laid any stress on this very important limitation of the usual theory.

We shall now produce a theory in which the only restrictions are that the thickness of the plate and the maximum displacement just mentioned are of smaller order than the radii of curvature of the bent middle surface. This will bring the plate theory to the same level as the Bernoulli-Eulerian theory of beams.

Let us assume that the xy plane touches the bent middle surface of the plate at some point, and that a particle of the middle surface which, in the unstrained state, would be at $x, y, 0$, is displaced to $x+u$, $y+v$, w. Let dx, dy denote the components of an element of length ds in the unstrained middle surface, and let ds_1 be the length of this element after strain. Then

$$(ds)^2 = (dx)^2 + (dy)^2$$

and $$(ds_1)^2 = (dx+du)^2 + (dy+dv)^2 + (dw)^2.$$

Now we may neglect $(du)^2$ and $(dv)^2$ since we shall retain the more important quantities du and dv, but we have no such reason for neglecting $(dw)^2$. Then

$$\begin{aligned}(ds_1)^2 &= (dx)^2 + (dy)^2 + 2dx\,du + 2dy\,dv + (dw)^2 \\ &= (ds)^2 + 2dx\,du + 2dy\,dv + (dw)^2.\end{aligned}$$

The extensional strain of ds_1 is

$$\begin{aligned}\frac{ds_1-ds}{ds}&=\frac{(ds_1)^2-(ds)^2}{ds(ds_1+ds)}\\&=\frac{(ds_1)^2-(ds)^2}{2(ds)^2}\\&=\frac{dx}{ds}\frac{du}{ds}+\frac{dy}{ds}\frac{dv}{ds}+\frac{1}{2}\left(\frac{dw}{ds}\right)^2. \quad . \quad . \quad . \quad (1)\end{aligned}$$

Now let ds make an angle θ with the x-axis.

Then $$\frac{dx}{ds}=\cos\theta, \quad \frac{dy}{ds}=\sin\theta.$$

Also $$du=\frac{\partial u}{\partial x}dx+\frac{\partial u}{\partial y}dy,$$

whence $$\frac{du}{ds}=\frac{\partial u}{\partial x}\cos\theta+\frac{\partial u}{\partial y}\sin\theta.$$

There are similar expressions for $\frac{dv}{ds}$ and $\frac{dw}{ds}$, and when these are substituted in equation (1), that equation gives the complete expression for the strain in any direction in the middle surface.

Putting $\theta=0$, we find that the strain in the direction of the x-axis is

$$\alpha=\frac{\partial u}{\partial x}+\frac{1}{2}\left(\frac{\partial w}{\partial x}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Putting $\theta=\frac{\pi}{2}$, we find that the strain in the y direction is

$$\beta=\frac{\partial v}{\partial y}+\frac{1}{2}\left(\frac{\partial w}{\partial y}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Again, the strains in the directions making angles 45° and −45° with the x-axis are

$$\alpha_1=\frac{1}{2}\left(\frac{\partial u}{\partial x}+\frac{\partial u}{\partial y}\right)+\frac{1}{2}\left(\frac{\partial v}{\partial x}+\frac{\partial v}{\partial y}\right)+\frac{1}{4}\left(\frac{\partial w}{\partial x}+\frac{\partial w}{\partial y}\right)^2,$$

$$\beta_1=\frac{1}{2}\left(\frac{\partial u}{\partial x}-\frac{\partial u}{\partial y}\right)-\frac{1}{2}\left(\frac{\partial v}{\partial x}-\frac{\partial v}{\partial y}\right)+\frac{1}{4}\left(\frac{\partial w}{\partial x}-\frac{\partial w}{\partial y}\right)^2.$$

Therefore $$\alpha_1-\beta_1=\frac{\partial u}{\partial y}+\frac{\partial v}{\partial x}+\frac{\partial w}{\partial x}\cdot\frac{\partial w}{\partial y}. \quad . \quad . \quad . \quad (4)$$

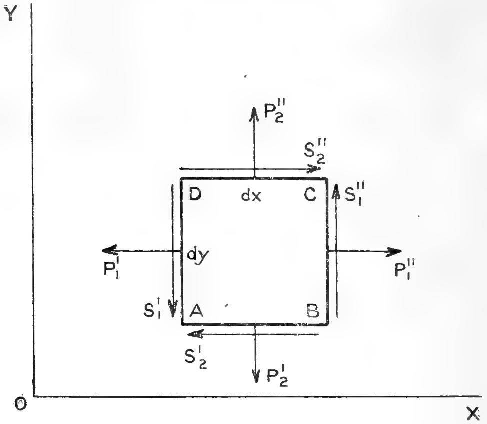
But it is easy to show that $(\alpha_1-\beta_1)$ is the *shear* strain of the element which was originally a rectangle with sides dx and dy in the middle surface. Let us call this shear strain γ.

Now let

E = Young's modulus for the material of the plate,
σ = Poisson's ratio,
n = the modulus of rigidity,
$2h$ = the thickness of the plate,
P_1, P_2 = the tensional stresses in the middle surface in the directions of dx and dy,
S = the shear stress in the middle surface on the faces on which P_1 and P_2 act.

The stresses P_1, P_2, S, are shown in fig. 1. It is understood that, as dx and dy approach zero, the stresses S_1', S_2', S_1'', S_2'', all approach the limit S.

Fig. 1.



Now, assuming that the tensional stress in the z-direction is negligible in comparison with P_1 and P_2, the usual equations of elasticity give

$$P_1 - \sigma P_2 = E\alpha = E\left\{\frac{\partial u}{\partial x} + \frac{1}{2}\left(\frac{\partial w}{\partial x}\right)^2\right\}, \quad . \quad . \quad . \quad . \quad (5)$$

$$P_2 - \sigma P_1 = E\beta = E\left\{\frac{\partial v}{\partial y} + \frac{1}{2}\left(\frac{\partial w}{\partial y}\right)^2\right\}, \quad . \quad . \quad . \quad . \quad (6)$$

$$S = n\gamma = n\left\{\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} + \frac{\partial w}{\partial x} \cdot \frac{\partial w}{\partial y}\right\}. \quad . \quad . \quad (7)$$

Since the stresses P_1, P_2, S, can be proved to be the mean values of the stresses at x, y, from $z = -h$ to $z = +h$, and since we are assuming that there are no external forces parallel to the middle surface of the plate, the equilibrium of the element $dx \times dy$ (fig. 1) requires that

$$2h(P_1'' - P_1')dy + 2h(S_2'' - S_2')dx = 0$$

and
$$2h(P_2'' - P_2')dx + 2h(S_1'' - S_1')dy = 0.$$

But
$$P_1'' - P_1' = \frac{\partial P_1}{\partial x}dx,$$

$$S_2'' - S_2' = \frac{\partial S}{\partial y}dy.$$

Therefore the above equations give

$$\frac{\partial P_1}{\partial x} + \frac{\partial S}{\partial y} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and
$$\frac{\partial P_2}{\partial y} + \frac{\partial S}{\partial x} = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If we now choose a function ϕ, such that

$$S = -E\frac{\partial^2 \phi}{\partial x \partial y}, \quad . \quad . \quad : \quad . \quad . \quad (10)$$

then equations (8) and (9) show that

$$P_1 = E\frac{\partial^2 \phi}{\partial y^2}; \quad P_2 = E\frac{\partial^2 \phi}{\partial x^2}. \quad . \quad . \quad . \quad . \quad (11)$$

Writing $\frac{E}{2(1+\sigma)}$ for n in equation (7), and then eliminating u and v from (5), (6), (7), we get

$$\frac{\partial^2}{\partial y^2}(P_1 - \sigma P_2) + \frac{\partial^2}{\partial x^2}(P_2 - \sigma P_1) - 2(1+\sigma)\frac{\partial^2 S}{\partial x \partial y}$$
$$= \tfrac{1}{2}E\left\{\frac{\partial^2}{\partial y^2}\left(\frac{\partial w}{\partial x}\right)^2 + \frac{\partial^2}{\partial x^2}\left(\frac{\partial w}{\partial y}\right)^2 - 2\frac{\partial^2}{\partial x \partial y}\left(\frac{\partial w}{\partial x} \cdot \frac{\partial w}{\partial y}\right)\right\},$$

That is,

$$\frac{\partial^4 \phi}{\partial x^4} + 2\frac{\partial^4 \phi}{\partial x^2 \partial y^2} + \frac{\partial^4 \phi}{\partial y^4} = \left(\frac{\partial^2 w}{\partial x \partial y}\right)^2 - \frac{\partial^2 w}{\partial x^2} \cdot \frac{\partial^2 w}{\partial y^2}.$$

Writing ∇^2 for $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$, this last equation may be written

$$\nabla^4 \phi = \left(\frac{\partial^2 w}{\partial x \partial y}\right)^2 - \frac{\partial^2 w}{\partial x^2} \cdot \frac{\partial^2 w}{\partial y^2}. \quad . \quad . \quad . \quad (12)$$

This is one of the equations of equilibrium of the plate. The other equation is a modified form of Poisson's equation, which form we shall now find.

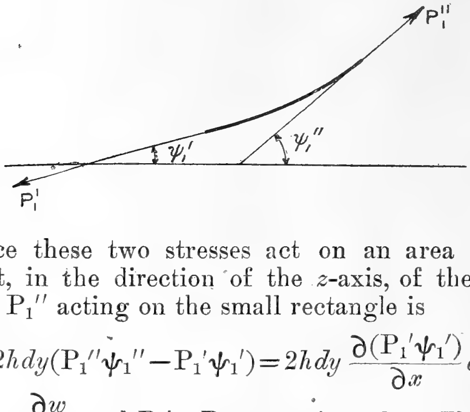
Let p denote the external force per unit area perpendicular to the plate. Then Poisson obtains the equation

$$\frac{2}{3}h^3\frac{E}{1-\sigma^2}\nabla^4 w=p. \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This equation gives the pressure supported by transverse shearing forces in the plate in the same way that the load on a beam is supported by the transverse shearing force. The stresses which we have denoted by P_1, P_2, S, are assumed to be zero in arriving at equation (13), but it is the object of this paper to show that these stresses cannot usually be zero. We must now correct this equation by taking into account the effect of the mean stresses P_1, P_2, and S.

Let P_1' (fig. 2) make a small angle $-\psi_1'$ with the plane of xy; and let P_1'' make an angle ψ_1'' with the same plane.

Fig. 2.



Then, since these two stresses act on an area $2hdy$, the component, in the direction of the z-axis, of the force due to P_1' and P_1'' acting on the small rectangle is

$$2hdy(P_1''\psi_1''-P_1'\psi_1')=2hdy\,\frac{\partial(P_1'\psi_1')}{\partial x}\,dx.$$

But $\psi_1'=\frac{\partial w}{\partial x}$, and $P_1'=P_1$ approximately. Therefore

$$2hdy(P_1''\psi_1''-P_1'\psi_1')=2h\frac{\partial}{\partial x}\left(P_1\frac{\partial w}{\partial x}\right)dx\,dy.$$

Thus the component force per unit area on the small rectangle in the direction of the z-axis due to P_1' and P_1'' is

$$2h\frac{\partial}{\partial x}\left(P_1\frac{\partial w}{\partial x}\right).$$

Likewise, due to P_2' and P_2'' there is a force per unit area in the same direction of amount

$$2h\frac{\partial}{\partial y}P_2\left(\frac{\partial w}{\partial y}\right).$$

Again, let $-\phi_1'$ denote the small angle which the force due to S_1' makes with the xy plane, and ϕ_1'' the corresponding angle for S_1''. Then the component force parallel to the z-axis due to these two forces is

$$2h\,dy(S_1''\phi_1''-S_1'\phi_1')=2h\,dy\frac{\partial(S_1'\phi_1')}{\partial x}dx.$$

But $\phi_1'=\dfrac{\partial w}{\partial y}$, and $S_1'=S_1=S$. Therefore

$$2h\,dy(S_1''\phi_1''-S_1'\phi_1')=2h\frac{\partial}{\partial x}\left(S\frac{\partial w}{\partial y}\right)dx\,dy.$$

Likewise, the corresponding force due to S_2' and S_2'' is

$$2h\frac{\partial}{\partial y}\left(S\frac{\partial w}{\partial x}\right)dx\,dy.$$

Therefore the total force per unit area in the direction of the z-axis due to all the mean stresses acting on the edges of the element $dx \times dy$ is

$$2h\left\{\frac{\partial}{\partial x}\left(P_1\frac{\partial w}{\partial x}\right)+\frac{\partial}{\partial y}\left(P_2\frac{\partial w}{\partial y}\right)+\frac{\partial}{\partial x}\left(S\frac{\partial w}{\partial y}\right)+\frac{\partial}{\partial y}\left(S\frac{\partial w}{\partial x}\right)\right\},$$

which, by means of equations (10) and (11), simplifies to

$$2hE\left\{\frac{\partial^2 w}{\partial x^2}\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2 w}{\partial y^2}\frac{\partial^2\phi}{\partial x^2}-2\frac{\partial^2 w}{\partial x\partial y}\cdot\frac{\partial^2\phi}{\partial x\partial y}\right\}.$$

This is the expression that must be added to p in equation (13), since, in that equation, p is the force per unit area in the direction of the z-axis which has to be supported by the transverse shear stresses. Thus the corrected form of Poisson's equation is

$$\frac{2}{3}\frac{Eh^3}{1-\sigma^2}\nabla^4 w-2hE\left\{\frac{\partial^2 w}{\partial x^2}\frac{\partial^2\phi}{\partial y^2}+\frac{\partial^2 w}{\partial y^2}\frac{\partial^2\phi}{\partial x^2}\right.$$
$$\left.-2\frac{\partial^2 w}{\partial x\partial y}\frac{\partial^2\phi}{\partial x\partial y}\right\}=p, \quad (14)$$

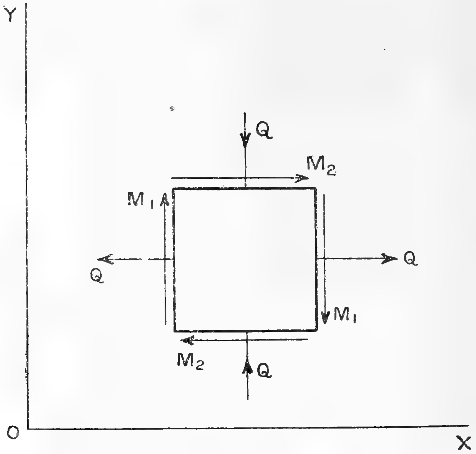
p being, in this equation, as in Poisson's equation, the external force per unit area.

This last equation takes the place of Poisson's equation. Since it contains two unknown functions, w and ϕ, it must be combined with equation (12), which we rewrite here,

$$\nabla^4\phi=\left(\frac{\partial^2 w}{\partial x\partial y}\right)^2-\frac{\partial^2 w}{\partial x^2}\cdot\frac{\partial^2 w}{\partial y^2}. \quad . \quad . \quad . \quad (12)$$

The residual stresses parallel to the middle surface after the mean stresses P_1, P_2, S, are taken away, are proportional to the distance from the middle surface. The residual tensions are equivalent to couples M_1, M_2, per unit length of

Fig. 3.



sections perpendicular to dx and dy respectively. The residual shear stresses give rise to equal couples Q per unit length about normals to the same two sections. These couples are represented by vectors in fig. 3, the right-handed screw system of representation being understood. The z-axis points upwards—that is, towards the reader. The expressions for these couples, which are correctly given by Poisson's theory, are

$$M_1 = C\left\{\frac{\partial^2 w}{\partial x^2} + \sigma\frac{\partial^2 w}{\partial y^2}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$M_2 = C\left\{\frac{\partial^2 w}{\partial y^2} + \sigma\frac{\partial^2 w}{\partial x^2}\right\}, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$Q = \frac{4}{3}h^3 n\frac{\partial^2 w}{\partial x \partial y}$$

$$= (1+\sigma)C\frac{\partial^2 w}{\partial x \partial y}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

where $$C = \frac{2}{3}\frac{Eh^3}{1-\sigma^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

It should be observed that the vector representing Q is along the outward normal for the pair of faces perpendicular to dx, and along the inward normal for the pair of faces perpendicular to dy.

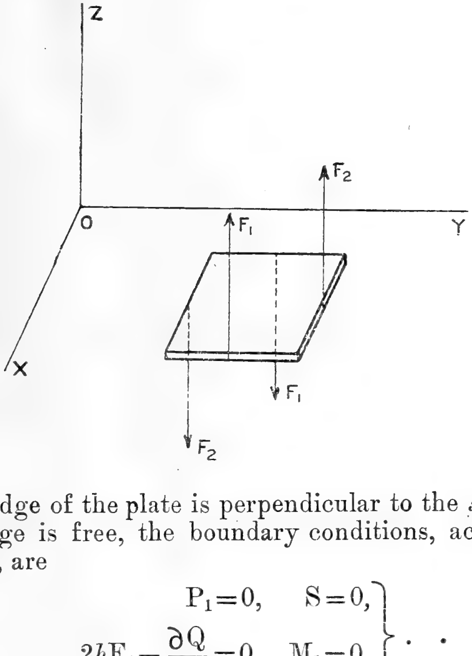
In addition to the above couples there are mean shear stresses F_1 and F_2, on the faces on which P_1 and P_2 act, these stresses acting in the direction of the z-axis. The magnitudes of these stresses are

$$F_1 = -\frac{C}{2h}\frac{\partial}{\partial x}(\nabla^2 w), \quad \ldots \quad (19)$$

$$F_2 = -\frac{C}{2h}\frac{\partial}{\partial y}(\nabla^2 w). \quad \ldots \quad (20)$$

The directions of these stresses are shown in fig. 4.

Fig. 4.



If the edge of the plate is perpendicular to the x-axis, and if this edge is free, the boundary conditions, according to Kirchhoff, are

$$\left.\begin{array}{ll} P_1=0, & S=0, \\ 2hF_1 - \dfrac{\partial Q}{\partial y} = 0, & M_1 = 0. \end{array}\right\} \quad \ldots \quad (21)$$

Poisson thought that F_1 and Q could be made to vanish separately at the boundary, but Kirchhoff showed that the solution of Poisson's differential equation does not contain enough arbitrary functions to satisfy all Poisson's boundary conditions. The reason why Poisson's boundary conditions cannot be satisfied is because his differential equation is derived from assumptions which are not even approximately true near the edge of the plate. The best physical explanation of this difficulty has been given by Professor Lamb in his paper "On the Flexure of an Elastic Plate" (Proceedings of the London Math. Soc. vol. xxi.).

Our new differential equations may require new boundary conditions. I think, however, that it is unlikely that we can satisfy more than the four boundary conditions of Kirchhoff, though this number depends upon the number of arbitrary functions, involving only real quantities, that are contained in the general values of w and ϕ satisfying equations (12) and (14). How many such functions there are I have to admit that I am unable to discover. Although some rules are given in the theory of partial differential equations concerning the number of arbitrary functions in the solution of a partial differential equation, these rules are not, I think, of any use for our purpose, because they make no distinction between functions with real arguments and functions with imaginary arguments. The theory tells us, for example, that the solution of the equation

$$\frac{\partial^2 V}{\partial x^2}+\frac{\partial^2 V}{\partial y^2}=0$$

contains two arbitrary functions. True, it does. But when we are confined to real quantities, these only amount to one, because the solution

$$V=f(x+iy)+F(x-iy)$$

degenerates into

$$V=f(x+iy)+f(x-iy).$$

I believe, however, that the number of boundary conditions is four in all cases, because it seems to be definitely four in some cases. Suppose, for example, that an unstrained plate has its edge completely fixed and clamped in its unstrained position. Then let any transverse forces be applied to the plate while the edge is still held. The problem in this case appears to be completely determinate, and the conditions at the edge are $u=0$, $v=0$, $w=0$, $\frac{\partial w}{\partial \nu}=0$, $d\nu$ being an element of the outward normal to the edge. This suggests that the functions w and ϕ are completely determined by the differential equations and four boundary conditions in one case, and therefore also in all other cases as well.

If we could solve equations (12) and (14) completely, we should have no trouble in deciding how many boundary conditions could be satisfied. But these equations are probably much too difficult to be solved completely. The introduction of the function ϕ has spoilt the linearity of Poisson's equations. It will be observed, however, that the equations are linear as far as ϕ is concerned. The physical interpretation of this is that, when one set of values of the stresses has been found for a given state of bending of the plate, any set of mean stresses P_1, P_2, and S, which would be in equilibrium if the plate were not bent, could be superposed on the set already obtained, and these new stresses would satisfy the differential equations. The pressure p is also altered since the added mean stresses, because they exist in a bent plate, could support a pressure on the surface, just as the tension in a membrane can support a pressure.

Owing to the complexity of the equations there are very few problems that we can solve directly; that is to say, there are few cases in which we can find w and ϕ from a given value of p. The inverse process of finding p when w is assumed offers, however, no great difficulty. We shall first express our equations in a form that applies to symmetry about the z-axis, and then make use of these equations to find p corresponding to a given w. We shall also solve the problem of a rectangular plate bent into a surface of revolution by forces applied at one pair of edges only. The second of the following problems illustrates the importance of the maximum displacement w in its effect on the pressure.

Symmetry about the z-axis.

Let $x^2+y^2=r^2$, and let us suppose that w and ϕ are functions of r only. Let P_1, M_1, etc., bear the same relation to the radius as they bore in the earlier equations to the x-axis. Then, u being the radial displacement, the two longitudinal strains are

$$\alpha=\frac{du}{dr}+\frac{1}{2}\left(\frac{dw}{dr}\right)^2,$$

$$\beta=\frac{u}{r},$$

and the shear strain is zero on an element with sides along and perpendicular to a radius.

The expressions for the mean stresses in terms of ϕ are

$$P_1=E\frac{1}{r}\frac{d\phi}{dr};\quad P_2=E\frac{d^2\phi}{dr^2};\quad S=0. \quad . \quad . \quad (22)$$

Also the principal curvatures of the middle surface are

$$\frac{d^2w}{dr^2} \text{ and } \frac{1}{r}\frac{dw}{dr}.$$

Consequently

$$M_1=C\left\{\frac{d^2w}{dr^2}+\frac{\sigma}{r}\frac{dw}{dr}\right\}, \quad . \quad . \quad . \quad . \quad (23)$$

$$M_2=C\left\{\frac{1}{r}\frac{dw}{dr}+\sigma\frac{d^2w}{dr^2}\right\}, \quad . \quad . \quad . \quad . \quad (24)$$

$$Q=0.$$

Again

$$\left.\begin{aligned}\nabla^2 w&=\frac{d^2w}{dr^2}+\frac{1}{r}\frac{dw}{dr}\\ &=\frac{1}{r}\frac{d}{dr}\left(r\frac{dw}{dr}\right)\\ \nabla^2\phi&=\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

It follows that

$$\left.\begin{aligned}F_1&=-\frac{C}{2h}\frac{d}{dr}(\nabla^2 w)\\ &=-\frac{C}{2h}\frac{d}{dr}\left\{\frac{1}{r}\frac{d}{dr}\left(r\frac{dw}{dr}\right)\right\}\\ F_2&=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad .\end{aligned}\right\} \quad . \quad . \quad . \quad (26)$$

Finally, the differential equations (12) and (14) become

$$\nabla^4\phi=-\frac{1}{r}\frac{dw}{dr}\cdot\frac{d^2w}{dr^2}:$$

that is,

$$\frac{d}{dr}\left(r\frac{d\psi}{dr}\right)=-\frac{dw}{dr}\cdot\frac{d^2w}{dr^2}, \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where
$$\psi=\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right);$$

and

$$\frac{2}{3}\frac{Eh^3}{1-\sigma^2}\nabla^4 w-2hE\frac{1}{r}\left(\frac{d^2w}{dr^2}\frac{d\phi}{dr}+\frac{dw}{dr}\frac{d^2\phi}{dr^2}\right)=p:$$

that is,

$$\frac{2}{3}\frac{Eh^3}{1-\sigma^2}\nabla^4 w-\frac{2hE}{r}\frac{d}{dr}\left(\frac{dw}{dr}\frac{d\phi}{dr}\right)=p. \quad . \quad . \quad . \quad (28)$$

Problem 1.—To find the stresses in a circular plate which is bent into the form of a piece of a spherical surface, of small solid angle, bounded by a circle.

Taking the xy plane touching the middle surface of the bent plate at its middle point, the deflexion is approximately

$$w=\frac{r^2}{2c},$$

c being the radius of the sphere.

Let a be written for the radius of the plate.

Then equation (27) becomes

$$\frac{d}{dr}\left(r\frac{d\psi}{dr}\right)=-\frac{r}{c^2}.$$

Integrating this once, we get

$$r\frac{d\psi}{dr}=-\frac{r^2}{2c^2}+\mathrm{H}.$$

The constant H must be zero because the other two terms in the equation are clearly zero when $r=0$. Therefore

$$\frac{d\psi}{dr}=-\frac{r}{2c^2},$$

whence $$\psi=-\frac{1}{4c^2}(r^2-b^2),$$

b^2 being the constant of integration.

Now we have got

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right)=-\frac{1}{4c^2}(r^2-b^2). \quad . \quad . \quad . \quad (29)$$

Integrating again, and omitting the new constant, which is obviously zero, we get

$$r\frac{d\phi}{dr}=-\frac{1}{4c^2}(\tfrac{1}{4}r^4-\tfrac{1}{2}b^2r^2). \quad . \quad . \quad . \quad . \quad (30)$$

Now the mean tensions are

$$\mathrm{P}_1=\frac{\mathrm{E}}{r}\frac{d\phi}{dr}=\frac{\mathrm{E}}{16c^2}(2b^2-r^2), \quad . \quad . \quad . \quad (31)$$

$$\mathrm{P}_2=\mathrm{E}\frac{d^2\phi}{dr^2}=\frac{\mathrm{E}}{16c^2}(2b^2-3r^2). \quad . \quad . \quad . \quad (32)$$

Let us now suppose that the radial tension is zero at the rim of the plate. That is,

$$\mathrm{P}_1=0 \text{ where } r=a,$$

or $$2b^2-a^2=0,$$

which gives the constant b^2.

Thus
$$P_1=\frac{E}{16c^2}(a^2-r^2), \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$P_2=\frac{E}{16c^2}(a^2-3r^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

Since
$$\nabla^4 w=0,$$
equation (28) gives
$$p=-\frac{2hE}{r}\frac{d}{dr}\left(\frac{r}{c}\frac{d\phi}{dr}\right)$$
$$=\frac{2hE}{c}\frac{1}{4c^2}(r^2-b^2)$$
$$=\frac{1}{4}\frac{hE}{c^3}(2r^2-a^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

It should be observed that the total thrust on the plate, namely,
$$\int_0^a 2\pi rp\,dr,$$
is zero, and also that the pressure p changes sign at the circle where $2r^2=a^2$. Moreover, the circumferential tension P_2 is positive where r is less than $\frac{a}{\sqrt{3}}$, and negative, that is, a thrust, where r is greater than $\frac{a}{\sqrt{3}}$.

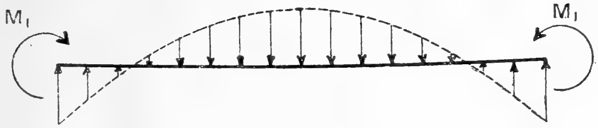
The mean shear stress F_1 is
$$F_1=-\frac{1}{3}\frac{Eh^2}{1-\sigma^2}\frac{d}{dr}(\nabla^2 w)$$
$$=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

The bending moments per unit length along and perpendicular to the radius are
$$M_1=C\left\{\frac{d^2w}{dr^2}+\frac{\sigma}{r}\frac{dw}{dr}\right\}$$
$$=C\left\{\frac{1}{c}+\frac{\sigma}{c}\right\}$$
$$=\frac{2Eh^3}{3(1-\sigma)c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$
$$M_2=M_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

We thus find that the middle surface of a circular plate will take the form of a portion of a spherical surface of radius c provided that a constant bending moment given by equation (37) is applied about each unit length of the rim, and that a variable pressure p given by equation (35) is applied to that surface of the plate which becomes the convex surface in the bent state.

Fig. 5 shows the way the pressure acts across a diametral section, and shows also the direction of the bending moment on the rim.

Fig. 5.



The usual Poisson or Kirchhoff method would make the pressure p and the tensions P_1 and P_2 zero, but would give the same values of M_1 and M_2.

In the solution we have just obtained we assumed that P_1 was zero at the edge of the plate, and this gave $b^2=2a^2$. If, however, P_1 is not zero, but has a positive value at the rim, we have only to leave b^2 in our equations, and for this case b^2 will be greater than $2a^2$. In this way a constant term will be added to each of the quantities P_1, P_2, and p. The added quantities are just the stresses and pressure in a stretched membrane which has no flexural rigidity.

Problem 2.—To find the pressure required, on the present theory, to produce the deflexion which a circular disk assumes according to Poisson's theory when subjected to a uniform pressure and supported without clamping at its edge.

According to Love ('Theory of Elasticity,' 3rd edition, Art. 314) or Morley ('Strength of Materials,' Art. 149), the deflexion of a disk of radius a due to a uniform pressure p_1 is

$$w=-H(2b^2r^2-r^4)+C, \quad . \quad . \quad . \quad . \quad (39)$$

where

$$H=\frac{3}{128}\frac{(1-\sigma^2)p_1}{Eh^3}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

and

$$b^2=\frac{3+\sigma}{1+\sigma}a^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

and C is a constant which depends on the position of the origin. If the xy plane touches the middle surface at the centre, then the constant C is zero. We shall find the pressure on the present theory which will produce the deflexion given in (39).

Equation (27) gives

$$\frac{d}{dr}\left(r\frac{d\psi}{dr}\right)=-\frac{dw}{dr}\frac{d^2w}{dr^2},$$

whence, by integration,

$$\begin{aligned} r\frac{d\psi}{dr}&=-\frac{1}{2}\left(\frac{dw}{dr}\right)^2\\ &=-8\mathrm{H}^2(b^2r-r^3)^2, \end{aligned}$$

the constant of integration being clearly zero.

Integrating again,

$$\psi=-8\mathrm{H}^2\left(\frac{1}{2}b^4r^2-\frac{1}{2}b^2r^4+\frac{1}{6}r^6\right)+\mathrm{B},$$

that is,

$$\frac{d}{dr}\left(r\frac{d\phi}{dr}\right)=-8\mathrm{H}^2\left(\frac{1}{2}b^4r^3-\frac{1}{2}b^2r^5+\frac{1}{6}r^7\right)+\mathrm{B}r.$$

Therefore

$$r\frac{d\phi}{dr}=-8\mathrm{H}^2\left(\frac{1}{8}b^4r^4-\frac{1}{12}b^2r^6+\frac{1}{48}r^8\right)+\frac{1}{2}\mathrm{B}r^2. \qquad (42)$$

Thus the radial tension is

$$\begin{aligned} \mathrm{P}_1&=\frac{1}{r}\frac{d\phi}{dr}\\ &=-8\mathrm{H}^2\left(\frac{1}{8}b^4r^2-\frac{1}{12}b^2r^4+\frac{1}{48}r^6\right)+\frac{1}{2}\mathrm{B}. \quad . \qquad (43) \end{aligned}$$

To make P_1 zero at the rim we must have

$$\frac{1}{2}\mathrm{B}=\frac{1}{6}\mathrm{H}^2a^2(6b^4-4b^2a^2+a^4). \quad . \quad . \quad . \qquad (44)$$

Again, by equation (28),

$$\begin{aligned} p&=\frac{2}{3}\frac{\mathrm{E}h^3}{1-\sigma^2}\nabla^4w-\frac{2\mathrm{E}h}{r}\frac{d}{dr}\left(\frac{dw}{dr}\frac{d\phi}{dr}\right)\\ &=p_1-\frac{2\mathrm{E}h}{r}\frac{d}{dr}\left(\frac{dw}{dr}\cdot\frac{d\phi}{dr}\right)\\ &=p_1+8\mathrm{HBE}h(b^2-2r^2)\\ &\quad-\frac{8}{3}\mathrm{H}^3\mathrm{E}hr^2(12b^6-20b^4r^2+20b^2r^4-5r^6) \quad . \qquad (45) \end{aligned}$$

Denoting the difference of the deflexions at the middle and the rim of the plate by w_0, and denoting the pressure at the centre by p_0, we get

$$\begin{aligned} w_0 &= \mathrm{H}a^2(2b^2-a^2) \\ &= \mathrm{H}a^4(2s-1), \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (46) \end{aligned}$$

where

$$s=\frac{b^2}{a^2}=\frac{3+\sigma}{1+\sigma}. \qquad . \quad . \quad . \quad . \quad . \quad . \qquad (47)$$

Also

$$\begin{aligned} p_0 &= p_1+8\mathrm{HBE}hb^2 \\ &= p_1+\frac{8}{3}\mathrm{H}^3\mathrm{E}ha^8(6s^3-4s^2+s) \\ &= p_1+\frac{8}{3}\mathrm{HE}hw_0{}^2\,\frac{6s^3-4s^2+s}{(2s-1)^2} \\ &= p_1\left\{1+\frac{1}{16}(1-\sigma^2)\frac{w_0{}^2}{h^2}\,\frac{6s^3-4s^2+s}{(2s-1)^2}\right\} \quad . \quad . \qquad (48) \end{aligned}$$

If $\sigma=\frac{1}{4}$, this becomes

$$p_0=p_1\left\{1+1\cdot 07\left(\frac{w_0}{2h}\right)^2\right\}, \quad . \quad . \quad . \quad . \qquad (49)$$

which shows that p_0 is approximately twice as great as p_1 if the maximum deflexion w_0 is equal to the thickness of the plate.

Moreover, at the rim of the plate, where $r=a$, we find that

$$p=p_1\left\{1-0\cdot 484\left(\frac{w_0}{2h}\right)^2\right\}; \quad . \quad . \quad . \qquad (50)$$

so that, if $w_0=2h$, the pressure at the edge of the plate is little more than half of p_1.

The preceding numerical results show how inaccurate are the usual Poisson equations when the maximum deflexion of the plate is of the same order as the thickness. As long as the maximum value of w is less than one-tenth of the thickness, it is clear that Poisson's equations give results that are as accurate as any that we can ever hope to get in such calculations. But for a body like a piece of tin bent so that the maximum deflexion is three or four times the thickness of the sheet, Poisson's method does not even give a pressure of the right order. In the example we have just worked out, if w_0 were only four times as great as $2h$, the pressure would vary from nearly $-7p_1$ at the rim to $17p_1$ at the centre, whereas Poisson's equations give a uniform pressure p_1 over the disk.

Problem 3.—A rectangular plate is bent into a part of a surface of revolution, which is nearly nearly cylindrical, by forces applied at one pair of opposite edges, the other pair of edges being circular arcs. To find the form of this surface.

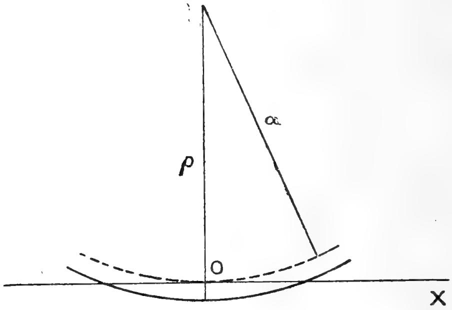
Let the xy plane be parallel to the tangent plane to the bent surface at its middle point. It is less troublesome to take the xy plane parallel to this tangent plane than actually coincident with it. Also let the y-axis be parallel to the axis of the surface of revolution, and the z-axis drawn towards the concave side of the cylinder.

The sections of the middle surface perpendicular to the y-axis are circular arcs with nearly equal radii. Let ρ be the radius of the arc at distance y from the xz plane, and let a denote the distance of the axis of revolution from the xy plane. Thus a is an approximate value of the radius of the circular arcs, since it is understood that the xy plane nearly coincides with the tangent plane at the centre of the bent middle surface.

Now let
$$\rho=a+w_1, \quad \ldots \ldots \quad (51)$$
where, clearly, w_1 is a function of y only.

Then the displacement of any point of the bent plate (fig. 6) at a small angular distance from the origin is approximately
$$w=-w_1+\frac{x^2}{2\rho}$$
$$=-w_1+\frac{x^2}{2a}. \quad \ldots \ldots \quad (52)$$

Fig. 6.



Hence
$$\frac{\partial^2 w}{\partial x^2}=\frac{1}{a}; \quad \frac{\partial^2 w}{\partial y^2}=-\frac{d^2 w_1}{dy^2}; \quad \frac{\partial^2 w}{\partial x \partial y}=0. \quad \ldots \quad (53)$$
$$\nabla^2 w=\frac{1}{a}-\frac{d^2 w_1}{dy^2}. \quad \ldots \ldots \quad (54)$$
$$\nabla^4 w=-\frac{d^4 w_1}{dy^4}. \quad \ldots \ldots \quad (55)$$

Now it is clear that the mean shear force S is zero because, in such a surface of revolution as we have assumed, the circumferential shear force on the circular sections is just as likely to act in one direction as in the other ; and since it cannot act in both at once, it must be zero. That is,

$$\frac{\partial^2\phi}{\partial x\partial y}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

whence $$\phi=f(y)+\mathrm{F}(x). \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

Moreover, the mean tensions P_1 and P_2 cannot be functions of x. But

$$P_2=E\frac{\partial^2\phi}{\partial x^2}=EF''(x)\,; \quad . \quad . \quad . \quad . \quad . \quad (58)$$

and since this cannot be a function of x it can only be a constant or zero. Then let

$$F''(x)=A.$$

It follows that $$F(x)=\tfrac{1}{2}Ax^2+B. \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

There can be no term containing the first power of x on account of the symmetry about the x-axis.

Since P_2 is constant, it has the same value at the edges of the plate as it has at any other point of the plate. As we are assuming that there are no actions on the circular edges of the plate, the stress P_2 must be zero, and therefore A must be zero. Moreover, the constant B can be merged into $f(y)$, so that

$$\phi=f(y). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60)$$

The equation for p now is

$$p=-\frac{2}{3}\frac{Eh^3}{1-\sigma^2}\frac{d^4w_1}{dx^4}-\frac{2Eh}{a}\frac{d^2\phi}{dy^2}. \quad . \quad . \quad . \quad . \quad (61)$$

Also the equation connecting w_1 and ϕ is

$$\frac{d^4\phi}{dy^4}=\frac{1}{a}\frac{d^2w_1}{dy^2},$$

from which $$\frac{d^2\phi}{dy^2}=\frac{1}{a}(w_1+C), \quad . \quad . \quad . \quad . \quad . \quad . \quad (62)$$

since symmetry requires no term involving the first power of y.

The constant C depends only on the position of the xy plane, and since we left this position indefinite in that it had only to be parallel to a certain tangent plane, we may put zero for C, provided we find finally that this leaves the xy plane somewhere very near the tangent plane mentioned.

Then

$$\frac{d^2\phi}{dy^2}=\frac{1}{a}w_1\,; \quad \ldots \ldots \quad (63)$$

and, substituting this in equation (61), we get

$$p=-\frac{2}{3}\frac{\mathrm{E}h^3}{1-\sigma^2}\frac{d^4w_1}{dy^4}-\frac{2\mathrm{E}h}{a^2}w_1. \quad \ldots \quad (64)$$

Now let $p=0$. Then

$$\frac{d^4w_1}{dy^4}=-4m^4w_1, \quad \ldots \ldots \quad (65)$$

where

$$4m^4=\frac{3(1-\sigma^2)}{h^2a^2}. \quad \ldots \ldots \quad (66)$$

The complete solution for w_1 is

$$\begin{aligned} w_1={}&\mathrm{H}\cosh my\cos my+\mathrm{K}\sinh my\sin my\\ &+\mathrm{H}_1\cosh my\sin my+\mathrm{K}_1\sinh my\cos my\,; \quad . \quad (67)\end{aligned}$$

but since w_1 is an even function of y we know that H_1 and K_1 are zero. Therefore

$$w_1=\mathrm{H}\cosh my\cos my+\mathrm{K}\sinh my\sin my. \quad . \quad (68)$$

Now let the width of the plate, that is, the dimension parallel to the y-axis, be $2l$. Then, in order to make the stresses zero at the circular edges of the bent plate, we must make

$$\left.\begin{aligned}\mathrm{M}_2=0\\ \mathrm{F}_2=0\end{aligned}\right\}\text{where } y=l. \quad \ldots \ldots \quad (69)$$

But

$$\begin{aligned}\mathrm{M}_2&=\mathrm{C}\left\{\frac{\partial^2w}{\partial y^2}+\sigma\frac{\partial^2w}{\partial x^2}\right\}\\ &=\mathrm{C}\left\{2m^2(\mathrm{H}\sinh my\sin my-\mathrm{K}\cosh my\cos my)+\frac{\sigma}{a}\right\}\end{aligned}$$

$$\ldots \quad (70)$$

and

$$\mathrm{F}_2=-\frac{\mathrm{C}m^3}{h}\left\{\begin{aligned}&\mathrm{H}(\cosh my\sin my+\sinh my\cos my)\\ &-\mathrm{K}(\sinh my\cos my-\cosh my\sin my)\end{aligned}\right\}. \quad (71)$$

Writing θ for ml, the conditions that M_2 and F_2 should be zero where $y=l$ are

$$-\mathrm{H}\sinh\theta\sin\theta+\mathrm{K}\cosh\theta\cos\theta=\frac{\sigma}{2m^2a},$$

$$\mathrm{H}(\cosh\theta\sin\theta+\sinh\theta\cos\theta)=\mathrm{K}(\sinh\theta\cos\theta-\cosh\theta\sin\theta).$$

Solving these for H and K, we get

$$\mathrm{H}=\frac{\sigma}{m^2a}\frac{\sinh\theta\cos\theta-\cosh\theta\sin\theta}{\sinh 2\theta+\sin 2\theta}, \quad . \quad . \quad (72)$$

$$\mathrm{K}=\frac{\sigma}{m^2a}\frac{\cosh\theta\sin\theta+\sinh\theta\cos\theta}{\sinh 2\theta+\sin 2\theta}, \quad . \quad . \quad (73)$$

wherein it should be noticed that

$$\frac{\sigma}{m^2a}=\frac{\sigma h}{\sqrt{3(1-\sigma^2)}}.$$

Thus

$$w_1=\frac{\sigma}{m^2a}\frac{1}{\sinh 2\theta+\sin 2\theta}\times$$
$$\left\{\begin{array}{l}(\sinh\theta\cos\theta-\cosh\theta\sin\theta)\cosh my\cos my\\+(\cosh\theta\sin\theta+\sinh\theta\cos\theta)\sinh my\sin my\end{array}\right\}, \quad (74)$$

and
$$w=\frac{x^2}{2a}-w_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (75)$$

As a particular case suppose ml, and therefore also my, is a small fraction. Then an approximate value of w_1, obtained by expanding the hyperbolic and circular functions, is

$$w_1=\frac{\sigma}{a}\left\{\frac{1}{2}y^2-\frac{1}{6}l^2\right\}. \quad . \quad . \quad . \quad . \quad (76)$$

This shows that the section of the middle surface by the yz plane is nearly a circle of radius $\frac{a}{\sigma}$. Thus our result gives the well-known anticlastic curvature of a bent rectangular rod.

Let us next suppose that ml is large, so that we may assume

$$\cosh\theta=\sinh\theta=\tfrac{1}{2}e^{\theta}\ ;\ \sinh 2\theta=\tfrac{1}{2}e^{2\theta}.$$

Then

$$w_1=\frac{\sigma e^{-\theta}}{m^2a}\left\{\begin{array}{l}(\cos\theta-\sin\theta)\cosh my\cos my\\+(\cos\theta+\sin\theta)\sinh my\sin my\end{array}\right\}. \quad . \quad (77)$$

In order to find the form of the surface near the free edges we can put

$$y=l-y',$$

and assume that y', the distance from the nearest free edge, is small compared with l. On doing this we get

$$w_1=\frac{\sigma e^{-\theta}}{m^2a}\left\{\begin{array}{l}\frac{1}{2}(\cos\theta-\sin\theta)e^{\theta-my'}\cos(\theta-my')\\+\frac{1}{2}(\cos\theta+\sin\theta)e^{\theta-my'}\sin(\theta-my')\end{array}\right\}$$

$$=\frac{\sigma}{2m^2a}e^{-my'}(\cos my'-\sin my')$$

$$=\sigma h\sqrt{\frac{2}{3(1-\sigma^2)}}e^{-my'}\cos\left(my'+\frac{\pi}{4}\right). \quad . \quad . \quad (78)$$

Thus we see that, when a broad rectangular plate is bent into a surface of revolution, small corrugations are formed on the bent surface, each crest and each trough forming a circular arc about the axis of revolution. However wide the plate may be, the maximum amplitude of the corrugations is approximately $\sqrt{\frac{2}{3}}\sigma h$, and the amplitude is smaller the nearer the wave lies to the middle circular arc of the bent plate.

When the plate is narrow, so that it approaches what we may call a beam or rod, only one small length of the oscillatory curve is comprised on the breadth of the plate, and this may be regarded as a circle of radius $\frac{a}{\sigma}$.

The extreme cases to which we have referred occur when ml is large and when ml is small respectively; that is, when l^2 is large and when l^2 is small compared with ah. When l^2 and ah are of the same order the complete expression for w_1 must be used.

If we had started with a sheet whose unstrained middle surface was that of a piece of a cylinder bounded by two generators and two circular arcs, it is easy to see that the preceding investigation can be adapted to give the strain when this cylinder is bent still further by forces and couples applied along the edges of the generators. If the radius of the cylinder before strain was b, and the approximate radius after strain a, then we have only to replace $\frac{1}{a}$ in the foregoing work by $\left(\frac{1}{a}-\frac{1}{b}\right)$. If l^2 is small in comparison with $\frac{abh}{b-a}$ the longitudinal section of the bent middle surface is approximately a circle with curvature $\sigma\left(\frac{1}{a}-\frac{1}{b}\right)$; whereas if l^2 is large in comparison with $\frac{abh}{b-a}$, there are many corrugations on the sheet, and the maximum amplitude is, as for a plane sheet, $\sigma h\sqrt{\frac{2}{3(1-\sigma^2)}}$.

In a paper read before the London Mathematical Society (Proceedings, vol. xxi. p. 142), Professor Lamb has obtained results for the bent cylinder which differ only in one respect from the results I have just indicated. The difference is that his results do not show the relation between h and the amplitude of the corrugations, and this is due to his tacit assumption that $(b-a)$ is small in comparison with b, a restriction which is quite unnecessary. He has a boundary condition which, written in terms of the symbols of this paper, has the form

$$\frac{d^2(\rho-b)}{dy^2}+\sigma\frac{\rho-b}{b^2}=0.$$

If this had been written in the more correct form

$$\frac{d^2(\rho-b)}{dy^2}+\sigma\left(\frac{1}{b}-\frac{1}{\rho}\right)=0,$$

and if, then, ρ had been replaced in the second term by its approximate value a, the condition would have been

$$\frac{d^2(\rho-b)}{dy^2}+\sigma\left(\frac{1}{b}-\frac{1}{a}\right)=0,$$

and this would have given the results indicated in the present paper.

In a later paper, read before the Manchester Literary and Philosophical Society [*], Professor Lamb worked out the problem of the flat plate bent into a surface of revolution by using an elementary method which has the advantage of showing clearly the physical actions taking place. His method was, however, a special one which did not show the connexion between this problem and the general theory in which the stretching of the middle surface is taken into account.

Problem 4.—The stretching of a circular membrane by a uniform pressure p over its area.

If the terms having a factor h are omitted from equation (14), we fall back on Poisson's equations. If, however, the term containing the factor h^3 were omitted, this would amount to assuming that the plate is much more effective in supporting pressure by means of its stretching than by

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[*] See also Phil. Mag. [5] vol. xxxi. p. 182.

means of its bending. That is to say, we should be assuming that the flexural rigidity is negligible and that the plate behaves as a membrane with a non-uniform tension. We are justified in neglecting the terms containing the factor h when w is everywhere small in comparison with h, and we are justified in neglecting the terms containing h^3 when h is small compared with the maximum value of w, unless the bent middle surface nearly coincides with a developable surface, in which case h must be small in comparison with the maximum deflexion measured from this developable surface.

We are now going to assume that a bent plate is symmetrical about the z-axis and that the terms containing h^3 in (14) are negligible. With these assumptions, equations (12) and (14) become

$$\frac{d}{dr}\left\{r\frac{d}{dr}(\nabla^2\phi)\right\}=-\frac{dw}{dr}\frac{d^2w}{dr^2}, \quad . \quad . \quad . \quad (79)$$

$$\frac{d}{dr}\left\{\frac{dw}{dr}\cdot\frac{d\phi}{dr}\right\}=-\frac{p}{2h\mathrm{E}}r. \quad . \quad . \quad . \quad (80)$$

One integration of each of these equations gives

$$r\frac{d}{dr}(\nabla^2\phi)=-\frac{1}{2}\left(\frac{dw}{dr}\right)^2. \quad . \quad . \quad . \quad . \quad (81)$$

and
$$\frac{dw}{dr}\cdot\frac{d\phi}{dr}=-\frac{p}{4h\mathrm{E}}r^2. \quad . \quad . \quad . \quad . \quad (82)$$

The constant of integration is zero in each case because $\frac{dw}{dr}$ is zero where r is zero for a circular plate with no central hole.

Now putting

$$\xi=r\frac{d\phi}{dr}, \quad \theta=\frac{1}{r}\frac{dw}{dr}, \quad s=r^2,$$

equations (81) and (82) become

$$\frac{d^2\xi}{ds^2}=-\frac{1}{8}\theta^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (83)$$

and
$$\theta\xi=-\frac{p}{4h\mathrm{E}}s. \quad . \quad . \quad . \quad . \quad . \quad . \quad (84)$$

When θ is eliminated from these the equation for ξ is

$$\frac{d^2\xi}{ds^2}=-\frac{1}{128}\frac{p^2}{h^2\mathrm{E}^2}\frac{s^2}{\xi^2}.$$

Next, putting

$$\left.\begin{aligned} s_1{}^4 &= s^4 \frac{p^2}{128h^8\mathrm{E}^2} \\ h^2\xi_1 &= \xi, \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (85)$$

and

we find that

$$\frac{d^2\xi_1}{ds_1{}^2} = -\frac{s_1{}^2}{\xi_1{}^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (86)$$

The complete solution of this equation contains two arbitrary constants, and we can see immediately how one of these constants is involved. For, putting

$$\xi_1 = \mathrm{C}^4 y, \quad s_1 = \mathrm{C}^3 x, \quad . \quad . \quad . \quad . \quad . \quad . \quad (87)$$

we find that (86) becomes

$$\frac{d^2y}{dx^2} = -\frac{x^2}{y^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

an equation which does not contain C. It follows that C is one of the arbitrary constants.

Now there is only one boundary condition in our present problem. It might be, for example, that P_1 has a given value when $r=a$, the radius of the boundary circle. The one constant C which occurs in the relations between x, y, s_1, ξ_1, is quite enough to enable us to satisfy this one condition. Then we need only a particular integral of equation (88) of the right type to solve our present problem.

Equation (88) has a solution expressing y in an infinite series of integral powers of x starting with the first power. This solution is

$$y = x - \frac{1}{2}x^2 - \frac{1}{6}x^3 - \frac{13}{144}x^4 - \frac{17}{288}x^5 - \frac{37}{864}x^6 - \frac{1205}{36288}x^7 \ldots \quad (89)$$

It is interesting to notice that, as long as x is a fairly small fraction, the series for y differs very little from

$$x - \frac{1}{2}x^2 - \frac{1}{6}x^3 - \frac{1}{12}x^4 - \frac{1}{20}x^5 - \ldots,$$

that is, from $\qquad -(1-x)\log_e(1-x).$

The radial tension is

$$\begin{aligned} \mathrm{P}_1 &= \frac{\mathrm{E}}{r}\frac{d\phi}{dr} = \frac{\mathrm{E}\xi}{r^2} \\ &= \frac{1}{4}(2p^2\mathrm{E}^2)^{\frac{1}{4}}\mathrm{C}\frac{y}{x} \\ &= \mathrm{P}_0\left\{1 - \frac{1}{2}x - \frac{1}{6}x^2 - \frac{13}{144}x^4 - \ldots\right\}, \quad . \quad (90) \end{aligned}$$

P_0 being, of course, the value of P_1 at the centre of the plate. Its value in terms of C is

$$P_0=\tfrac{1}{4}(2p^2E^2)^{\frac{1}{4}}C. \qquad (91)$$

Also

$$x=\frac{s_1}{C}=\frac{1}{512}\frac{p^2Er^2}{P_0{}^3h^2}$$

$$=\frac{Hr^2}{P_0{}^3}\text{ say}. \qquad (92)$$

Let the radius of the plate be a, and let $P_1=T$ at the rim. Then

$$T=P_0\left\{1-\frac{1}{2}\frac{Ha^2}{P_0{}^3}-\frac{1}{6}\frac{H^2a^4}{P_0{}^6}-\frac{13}{144}\frac{H^3a^6}{P_0{}^9}-\ldots\right\}. \qquad (93)$$

If P_0 is given, this equation determines T directly; but if T is given, it determines P_0 indirectly. Inverting the series to give P_0 in terms of T, we get

$$P_0=T\left\{1+\frac{1}{2}\frac{Ha^2}{T^3}-\frac{1}{3}\frac{H^2a^4}{T^6}+\frac{55}{144}\frac{H^3a^6}{T^9}\ldots\ldots\right\}. \qquad (94)$$

The first approximation, namely

$$P_0=T, \qquad (95)$$

makes P_1 constant over the plate, which is the usual assumption in dealing with stretched membranes.

The second approximation is

$$P_0=T+\frac{1}{2}\frac{Ha^2}{T^2}, \qquad (96)$$

and the corresponding value of the radial tension at any point is

$$P_1=P_0-\frac{1}{2}\frac{Hr^2}{P_0{}^2}$$

$$=T+\frac{1}{2}\frac{H}{T^2}(a^2-r^2)$$

$$=T+\frac{1}{1024}\frac{p^2E}{h^2T^2}(a^2-r^2). \qquad (97)$$

The third approximations are

$$P_0=T+\frac{1}{2}\frac{Ha^2}{T^2}-\frac{1}{3}\frac{H^2a^4}{T^5}. \qquad (98)$$

and

$$P_1=T+\frac{1}{2}\frac{H}{T^2}(a^2-r^2)-\frac{1}{6}\frac{H^2}{T^5}(a^2-r^2)(2a^2-r^2). \qquad (99)$$

Equations (94) to (99) are valid only on the assumption that T and P_0 are nearly equal. We shall now consider the possibility of a zero value of P_1.

Equation (88) shows that $\frac{dy}{dx}$ decreases as x increases for all values of x and y. It follows that y must finally become zero, and it is easy to see that, starting with finite values of y and $\frac{dy}{dx}$, y becomes zero for a finite value of x, and therefore for a finite value of r. Since P_1 is proportional to $\frac{y}{x}$, it follows that P_1 vanishes for a finite value of r, and equation (82) shows that $\frac{dw}{dr}$ is infinite when P_1 is zero. This is, of course, a physical impossibility, and, moreover, the whole theory fails when $\frac{dw}{dr}$ is not a small fraction. Nevertheless it is interesting to consider this extreme case.

If P_1 is zero, the following equation must be satisfied:

$$\frac{y}{x}=1-\frac{1}{2}x-\frac{1}{6}x^2-\frac{13}{144}x^3-\frac{17}{288}x^4-\ldots=0. \qquad (100)$$

Now we have already noticed the good agreement between the earlier terms in the series for y and those in the expansion of $-(1-x)\log(1-x)$. If we could be sure that all the remaining coefficients of the series in equation (100) were less than the corresponding coefficients in the expansion of

$$-\frac{1-x}{x}\log_e(1-x),$$

as they certainly promise to be, then we could safely assert that the root x_1 of (100) is less than the root of

$$-\frac{(1-x)}{x}\log_e(1-x)=0,$$

which latter root is unity.

It is not very difficult to get a closer approximation to the value of x_1, as can be seen in the following process.

If the expression $x\left(1-\frac{7}{6}x\right)^{3/7}$ be expanded in powers of x, it will be seen that the first three powers of x have the same coefficients as the corresponding terms in equation (89). Moreover, the curve represented by

$$y=x\left(1-\frac{7}{6}x\right)^{3/7} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (101)$$

has the same general characteristics as the curve represented by (89); for equation (88) shows that the curve determined by that equation meets the x-axis perpendicularly at the point where y is zero and x is not zero, and the curve represented by (101) has this same characteristic.

Now, assuming that y is correctly given by (101), and substituting this value for y on the right-hand side of equation (88), we get

$$\frac{d^2y}{dx^2}=-\left(1-\frac{7}{6}x\right)^{-6/7}.$$

Solving this and adjusting the constants so that y and $\frac{dy}{dx}$ have the same values when $x=0$ as are given by (89), we find

$$y=\frac{9}{2}-\frac{9}{2}\left(1-\frac{7}{6}x\right)^{8/7}-5x. \quad . \quad . \quad . \quad (102)$$

The expansion of the right-hand side of this last equation gives

$$y=x-\frac{1}{2}x^2-\frac{1}{6}x^3-\frac{13}{144}x^4-\frac{17\frac{1}{3}}{288}x^5-\frac{39}{864}x^6-\frac{1326}{36288}x^7-; \quad . \quad . \quad . \quad . \quad (103)$$

an equation which coincides almost exactly with (89). For values of x less than unity, the difference between the two values of y is certainly very small. Then we may assume that the value of y given by (89) is approximately the same as that given by (102).

To find an approximate value of x_1 we have therefore to solve the equation

$$\frac{9}{2}-5x=\frac{9}{2}\left(1-\frac{7}{6}x\right)^{8/7}. \quad . \quad . \quad . \quad (104)$$

A close approximation to the root is

$$x_1=0{\cdot}883.$$

It follows then that P_1 is zero or very small when r has the value r_1 given by the equation

$$\frac{1}{512}\frac{p^2Er_1^{\,2}}{P_0^{\,3}h^2}=0{\cdot}883. \quad . \quad . \quad . \quad . \quad (105)$$

Thus we see that the complete membrane determined by our differential equations (in which certain physical difficulties are ignored) has an asymptotic cylinder, the radius of which is given by (105). A section through the middle of the membrane would have some resemblance to the curve of a catenary of uniform strength.

If ϕ is zero or negligible the equations in this paper reduce to the usual Poisson equations for thin plates. Now it follows from equation (12) that ϕ can be zero provided that

$$\left(\frac{\partial^2 w}{\partial x \partial y}\right)^2 - \frac{\partial^2 w}{\partial x^2} \cdot \frac{\partial^2 w}{\partial y^2} = 0. \quad . \quad . \quad . \quad . \tag{106}$$

But this is precisely the condition that the bent middle surface should be a developable surface. When ϕ is zero the middle surface is unstretched, and now we find from our equations, what is quite obvious from geometry, that a plane sheet can be bent into a developable surface without the stretching or shrinking of any of its elements.

If the expression on the left-hand side of equation (106) is small but not zero, it is still possible that ϕ be so small that Poisson's equations are approximately true. The examples we have worked out indicate that this condition is satisfied if w is everywhere small in comparison with the thickness of the plate. Since the expression in (106) is of the second order in w it is clear that ϕ depends on w^2 rather than on w. The condition that ϕ should be negligible will still be satisfied if the deflexion of the middle surface, measured from some developable surface, is small compared with the thickness of the plate. The third problem worked out above supplies an example of this.

X. *On the Transverse Vibrations of Bars of Uniform Cross-Section.* *By* Prof. S. P. Timoshenko [*].

§ 1. In a paper recently published in this Magazine [†], I have dealt with the corrections which must be introduced into the equation for transverse vibrations of a prismatic bar, viz.,

$$\mathrm{EI}\,\frac{\partial^4 y}{\partial x^4} + \frac{\rho\Omega}{g}\,\frac{\partial^2 y}{\partial t^2} = 0, \quad . \quad . \quad . \quad . \quad . \tag{1}$$

in order that the effects of "rotatory inertia" and of the deflexion due to shear may be taken into account.

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[*] Communicated by Mr. R. V. Southwell, M.A.

[†] Phil. Mag. vol. xli. pp. 744-746.

In equation (1)

EI denotes the flexural rigidity of the bar,

Ω the area of the cross-section

and $\frac{\rho}{g}$ the density of the material.

It was shown that the correction for shear, in a representative example, was four times as important as the correction for "rotatory inertia," and that both corrections are unimportant if the wave-length of the transverse vibrations is large in comparison with the dimensions of the cross-section.

In the present paper, an exact solution of the problem is given in the case of a beam of rectangular section, of which the breadth is great or small compared with the depth, so that the problem is virtually one of plane strain or of plane stress. The results are compared with those of my former paper, and confirm the conclusions which were there obtained.

§ 2. When the problem is one of plane strain (so that w is constant), we have to solve the equations *

$$\left.\begin{array}{l}(\lambda+2\mu)\nabla^2\Delta+\rho p^2\Delta=0, \\ \text{and} \qquad \mu\nabla^2\varpi+\rho p^2\varpi=0, \\ \text{where } \Delta \text{ denotes the cubical dilatation } \left(\frac{\partial u}{\partial x}+\frac{\partial v}{\partial y}\right), \\ \varpi \quad \text{,,} \quad \text{the rotation } \frac{1}{2}\left(\frac{\partial v}{\partial x}-\frac{\partial u}{\partial y}\right), \\ \text{and} \quad \nabla^2 \quad \text{,,} \quad \text{the operator } \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right).\end{array}\right\} \qquad (2)$$

Taking the x-axis in the direction of the central line, and choosing for Δ an even and for ϖ an uneven function of y, we may write

$$\left.\begin{aligned}\Delta &= \mathrm{A}\sin\alpha x\sinh my\cos pt, \\ 2\varpi &= \mathrm{B}\cos\alpha x\cosh ny\cos pt,\end{aligned}\right\} \quad . \quad . \quad . \quad (3)$$

where A and B are undetermined coefficients,

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* A. E. H. Love, 'Theory of Elasticity,' §§ 14 (d) and 204.

$$\left.\begin{array}{ll}
m = \alpha\sqrt{1-\left(\frac{V}{V_1}\right)^2}. & \\
n = \alpha\sqrt{1-\left(\frac{V}{V_2}\right)^2}, & \\
V = \frac{p}{\alpha}, & \text{denotes the velocity of waves of transverse vibration,} \\
V_1 = \sqrt{\frac{\lambda+2\mu}{\rho}}, & \text{denotes the velocity of waves of dilatation,} \\
\text{and} \quad V_2 = \sqrt{\frac{\mu}{\rho}}, & \text{denotes the velocity of waves of distortion.}
\end{array}\right\} \quad (4)$$

It is easily verified that equations (3) are satisfied by the expressions

$$\left.\begin{array}{l}
u = \cos ax\,(M\sinh my + N\sinh ny)\cos pt, \\
v = \sin ax\left(M\frac{m}{\alpha}\cosh my + N\frac{\alpha}{n}\cosh ny\right)\cos pt,
\end{array}\right\}$$

and the conditions that the boundaries ($y = \pm c$) are free from traction give us

$$\left.\begin{array}{ll}
[(\lambda+2\mu)m^2-\lambda\alpha^2]\,M\sinh mc + 2\mu\alpha^2 N\sinh nc & = 0, \\
\text{and} \quad 2mnM\cosh mc + (\alpha^2+n^2)N\cosh nc & = 0.
\end{array}\right\}$$

Hence, by eliminating the ratio M/N, we obtain the "frequency equation" in the form *

$$4\mu\alpha^2 mn\tanh nc = (\alpha^2+n^2)\,[(\lambda+2\mu)m^2-\lambda\alpha^2]\tanh mc\,;$$

whence, denoting the length of the waves by l, and putting $V/V_1 = f$, $V/V_2 = h$, we have

$$4\sqrt{(1-f^2)(1-h^2)}\tanh\left(\frac{2\pi c}{l}\sqrt{1-h^2}\right)$$
$$= (2-h^2)^2\tanh\left(\frac{2\pi c}{l}\sqrt{1-f^2}\right). \quad (5)$$

If V be given, the corresponding value of the ratio $l/2c$

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* This "frequency equation" was found by Prof. P. Ehrenfest and myself in collaboration. The solution given in this paper is my own.

can be calculated from this equation. Some results are given in the table below *.

h =	0·5	0·7	0·9	0·9165	0·9192
$l/2c$ =	4·8	2·5	0·75	0·47	0·30

§ 3. In the case of long waves, the velocity V is inversely proportional to the length l, but as l diminishes it can be seen, from equation (5), to approach a limit which is lower than V_2, and can be found from the relation

$$4\sqrt{(1-f^2)(1-h^2)} = (2-h^2)^2.$$

This limit is the velocity of the "Rayleigh waves" †. If we put $\lambda=\mu$, we obtain, in the limit, $V=0{\cdot}9194\,V_2$.

As the wave-length l increases, the arguments of the hyperbolic functions in equation (5) decrease, and we can employ the ascending series. If we limit our attention to the first three terms, we may write equation (5) in the form

$$a(\alpha c)^4+b(\alpha c)^2+d=0, \quad . \quad . \qquad (6)$$

where

$$\left.\begin{aligned} a &= \tfrac{2}{15}[4(1-h^2)^3-(2-h^2)^2(1-f^2)^2], \\ b &= -\tfrac{1}{3}[4(1-h^2)^2-(2-h^2)^2(1-f^2)], \\ d &= -h^4. \end{aligned}\right\} \quad . \quad . \qquad (7)$$

When αc is very small, we can obtain a first approximation by neglecting the first term in (6) and putting

$$(\alpha c)^2 = -\frac{d}{b}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

This approximation will be

$$(\alpha c)^2 = \frac{3}{4}\frac{h^2(\lambda+2\mu)}{\lambda+\mu}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

whence

$$V^2 = \tfrac{4}{3}(\alpha c)^2\frac{\mu(\lambda+\mu)}{\rho(\lambda+2\mu)}, \quad . \quad . \quad . \qquad (10)$$

and

$$p^2 = \alpha^2V^2 = \alpha^4c^2\frac{4\mu(\lambda+\mu)}{3\rho(\lambda+2\mu)}. \quad . \quad . \quad . \qquad (11)$$

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* In these calculations, σ has been taken to be 0·25.

† A. E. H. Love, *op. cit.* § 214.

Replacing λ by the quantity

$$\lambda' = \frac{2\lambda\mu}{\lambda + 2\mu}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

we should obtain the corresponding approximate solution for the case of plane stress, and it is easily verified that this is equivalent to the solution of equation (1).

Proceeding to a further approximation in the case of plane strain, we observe that the quantity d in (6) is small in comparison with a and b, and that the solution of this equation can therefore be written as follows:

$$(\alpha c)^2 = -\frac{d}{b}\left(1 + \frac{a}{b} \cdot \frac{d}{b}\right). \quad . \quad . \quad . \quad . \quad (13)$$

The second term in the bracket on the right-hand side is a small correction. In calculating it, we may take for $\frac{d}{b}$ the first approximation (8), and in the expression for a/b we may retain the terms of the order h^2 and f^2 only. We then have

$$\frac{a}{b} \cdot \frac{d}{b} = \tfrac{4}{5}(\alpha c)^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The first term on the right of (13) must be calculated more exactly. Retaining in the expression for b terms of the order f^4 and h^4, and substituting for V the first approximation (10), we have

$$-\frac{d}{b} = \tfrac{3}{4} h^2 \frac{\lambda + 2\mu}{\lambda + \mu} \left[\frac{1}{1 - \frac{1}{3}(\alpha c)^2 \frac{3\lambda + 2\mu}{\lambda + 2\mu}} \right] \quad . \quad . \quad (15)$$

Substituting from (14) and (15) in (13), and neglecting small quantities of higher order, we obtain

$$(\alpha c)^2 = \tfrac{3}{4} h^2 \frac{\lambda + 2\mu}{\lambda + \mu} \left[1 + \tfrac{1}{3}(\alpha c)^2 \left(\frac{3\lambda + 2\mu}{\lambda + 2\mu} + \frac{12}{5} \right) \right],$$

or

$$p^2 = \frac{\alpha^4 c^2}{3} \frac{4\mu(\lambda + \mu)}{(\lambda + 2\mu)} \left[1 - \tfrac{1}{3}(\alpha c)^2 \left(\frac{3\lambda + 2\mu}{\lambda + 2\mu} + \frac{12}{5} \right) \right]. \quad . \quad . \quad . \quad (16)$$

§ 4. The square brackets in (16) contain the required corrections to (11). These correspond principally to the effects of "rotatory inertia" and of shearing force, and could have been obtained with sufficient accuracy from the equation for transverse vibrations of rods, if this is supplemented in the manner explained in my previous paper, where the correction to the frequency p was given in the form of a multiplying term of amount *

$$\left[1-\frac{1}{2}\frac{\pi^2k^2}{\mathrm{L}^2}\left(1+\frac{\mathrm{E}}{\lambda\mathrm{C}}\right)\right]. \quad . \quad . \quad . \quad . \quad (17)$$

In this expression, π/L is equivalent to the α of the present paper, and $k^2=c^2/3$. λ is a constant relating the shearing force with the angle of shear at the section considered: its value for a rectangular section (if we make use of the experimental results of L. N. G. Filon †) is 8/9. The ratio E/C must be replaced, for comparison with our present problem of plane strain, by the quantity $\frac{4(\lambda+\mu)}{\lambda+2\mu}$ (in the notation of the present paper). We then have from (17), in our present notation, as the correcting factor required in the expression for the *square of the frequency*,

$$\left[1-\tfrac{1}{3}(\alpha c)^2\left(1+\frac{3}{2}\frac{\lambda+\mu}{\lambda+2\mu}\right)\right].$$

With $\sigma=0{\cdot}25$, or $\lambda=\mu$, the correction to p^2, given by (17), is thus

$$[1-\tfrac{4}{3}(\alpha c)^2], \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

whilst (16) gives

$$[1-\tfrac{61}{45}(\alpha c)^2]. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

§ 5. This close agreement gives us some confidence in applying the approximate solution of my earlier paper to other shapes of cross-section. We take, for example, the case of a circular cross-section ‡: the exact solution may be written in the form

$$\mathrm{V}=\frac{\pi c}{l}\sqrt{\frac{\mathrm{E}}{\rho}}\left[1-\frac{\pi^2c^2}{3l^2}\left(\frac{7}{2}+\frac{\mathrm{E}}{\mu}-\frac{\mu}{\mathrm{E}}\right)\right], \quad . \quad . \quad . \quad (20)$$

where c denotes the radius of the cross-section; whilst the methods of my earlier paper would give

$$\mathrm{V}=\frac{\pi c}{l}\sqrt{\frac{\mathrm{E}}{\rho}}\left[1-\frac{\pi^2c^2}{2l^2}\left(1+\frac{\mathrm{E}}{\kappa\mu}\right)\right], \quad . \quad . \quad . \quad (21)$$

where κ is the "shear constant" previously denoted by λ.

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* *Cf.* equation (13) of the paper referred to.

† A. E. H. Love, *op. cit.* § 245.

‡ See Pochhammer, *Journal f. d. reine u. angw. Math.* Bd. lxxxi. p. 335 (1876).

If we put

$$\lambda = \mu\,; \quad 1/\kappa = \tfrac{3}{4}\times 1{\cdot}40 = 1{\cdot}05,$$

the correcting factor found from (20) will be $1{\cdot}87\,\frac{\pi^2c^2}{l^2}$, and from (21) will be $1{\cdot}81\,\frac{\pi^2c^2}{l^2}$. Thus we have again obtained very satisfactory results from the approximate formula (17).

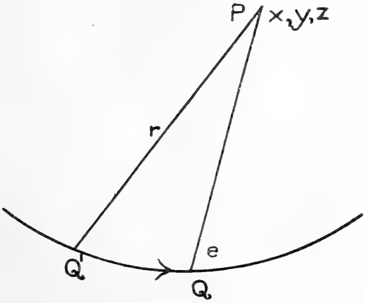
§ 6. In this investigation of transverse vibrations we have taken the expressions (3) for Δ and ϖ. By taking the even function of y for Δ and the uneven function for ϖ, we may obtain the solution of the problem of longitudinal vibrations.

Zagreb,
January 26, 1921.

XI. *On Scalar and Vector Potentials due to Moving Electric Charges.* *By* Prof. A. ANDERSON [*].

IN the Philosophical Magazine (March, 1921) Prof. A. Liénard criticises my paper on "A method of finding Scalar and Vector Potentials due to Motion of Electric Charges" (Phil. Mag. August 1920). The criticism, though just, touches only a slight error in notation; the results of the paper are not affected thereby. The last part of my paper is very much condensed and perhaps, on that account, unintelligible, and the object of the present communication is to make the argument fuller, and, I hope, clearer.

Fig. 1.



In fig. 1, Q is the position at time t of a moving charge e, and Q' is a point moving in the path of Q—the companion

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[*] Communicated by the Author.

point of Q, we may call it. The position of Q′ is the same as that of Q at a time $t-\frac{r}{c}$, where r is the distance of Q′ from a point P in the field whose coordinates are x, y, z.

I proved in the paper referred to that, if

$$A=\frac{F\left(t-\frac{r}{c}\right)}{r\left(1-\frac{u_r}{c}\right)},$$

where $F\left(t-\frac{r}{c}\right)$ is any function of $t-\frac{r}{c}$ and u_r is the resolved part along Q′P of the velocity of Q when at Q′,

$$\nabla^2 A-\frac{1}{c^2}\frac{\partial^2 A}{\partial t^2}=0 \quad \text{at P.}$$

The velocity of Q′ is, of course, not the same as the velocity of Q when at Q′, the latter is a function of $t-\frac{r}{c}$, the former is not.

Suppose now that there is a distribution of electricity in motion. The whole distribution may be conceived as divided up into elemental charges. Let dq be the element charge at Q. It is clear that, if

$$A=\int\frac{dq}{r\left(1-\frac{u_r}{c}\right)},$$

where r is the distance of Q′ the companion point of Q from any point P, and u_r the resolved part of the velocity of dq when at Q′ along Q′P,

$$\nabla^2 A-\frac{1}{c^2}\frac{\partial^2 A}{\partial t^2}=0 \quad \text{at P,}$$

if the density of the moving electric distribution be zero at P. If the distribution is a volume and surface distribution on moving bodies unaltered by the motion of the bodies, we may write

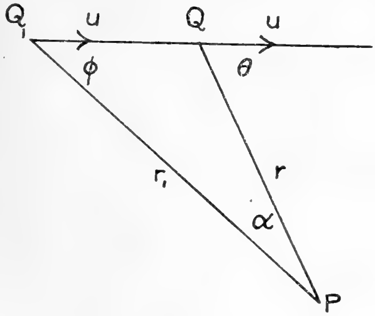
$$A=\int\frac{\rho\, dT}{r\left(1-\frac{u_r}{c}\right)}+\int\frac{\sigma\, dS}{r\left(1-\frac{u_r}{c}\right)},$$

where dT and dS are elements of volume and surface, ρ and σ

being the volume and surface densities, and the denominators of the integrands having the same meanings as before.

But if there is electricity at the point P either at rest or in motion, $\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2}$ no longer vanishes, and we must find what its value is. If we imagine a small sphere of electricity removed, the expression becomes zero at P. Hence its actual value at P is that due to this sphere of moving electricity. But we shall see that, if the radius of the sphere diminishes without finite limit both A and $\frac{\partial^2 A}{\partial t^2}$ tend to zero. Hence the value of the expression at P is the limiting value of $\nabla^2 A$ at P due to the sphere, when its radius is made to diminish indefinitely. Inside this small sphere the velocity of the electricity may be regarded as uniform and as having the value that it has at P.

Fig. 2.



Let an element of electricity dq at Q at the time t be moving with uniform velocity u in the straight line Q_1Q (fig. 2). Its companion point Q_1 is the position of dq at the time $t - \frac{Q_1P}{c}$, and the element contributed to the integral A by dq is

$$\frac{dq}{PQ_1 - PQ_1\frac{u\cos\phi}{c}} = \frac{dq}{PQ_1 - QQ_1\cos\phi} = \frac{dq}{PQ\cos\alpha}.$$

But

$$\frac{\sin\alpha}{\sin\theta} = \frac{QQ_1}{PQ_1} = \frac{u}{c}.$$

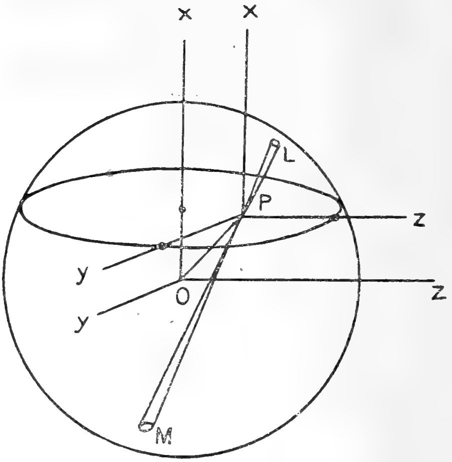
Hence the element contributed to the integral A is

$$\frac{dq}{r\sqrt{1-\frac{u^2}{c^2}\sin^2\theta}},$$

where $r=$PQ is the distance of the actual charge from P and θ is the angle which the direction of motion makes with QP.

With the aid of this expression we must now find the value of A for any point P inside a sphere of radius a whose centre is O, the electricity in it being uniformly distributed and of density ρ, with a uniform velocity u parallel to the axis of z.

Fig. 3.



In fig. 3, let OP$=b$, and let the direction cosines of OP be l, m, n. Also, let axes be drawn through P parallel to the rectangular axes through O. Draw a cone of small solid angle $d\omega$ having its vertex at P and intersecting the sphere at L and M. We first find the part of the integral A contributed by this cone.

This is

$$d\omega\int\frac{\rho\, r^2 dr}{r\sqrt{1-\frac{u^2}{c^2}\sin^2\theta}}=\rho\cdot\frac{r_1{}^2+r_2{}^2}{2}\cdot\frac{d\omega}{\sqrt{1-\frac{u^2}{c^2}\sin^2\theta}},$$

where PL$=r_1$, PM$=r_2$, and $\theta=$angle LPz. Let the plane

LPz intersect the plane xPy in a line which makes an angle ϕ with Px. Denoting the angle OPM by α, we have

$$r_1^2+r_2^2=4b^2\cos^2\alpha+2(a^2-b^2)$$
$$=4b^2[n\cos\theta+l\sin\theta\cos\phi+m\sin\theta\sin\phi]^2+2(a^2-b^2).$$

Hence

$$\mathrm{A}=\rho\iint\frac{\{2b^2(n\cos\theta+l\sin\theta\cos\phi+m\sin\theta\sin\phi)^2+a^2-b^2\}\sin\theta\,d\theta\,d\phi}{\sqrt{1-\frac{u^2}{c^2}\sin^2\theta}},$$

or, if the co-ordinates of P in reference to the axes through O are x, y, z,

$$\mathrm{A}=\rho\iint\frac{\{2(z\cos\theta+x\sin\theta\cos\phi+y\sin\theta\sin\phi)^2+a^2-x^2-y^2-z^2\}\sin\theta\,d\theta\,d\phi}{\sqrt{1-\frac{u^2}{c^2}\sin^2\theta}},$$

the limits of ϕ being $-\frac{\pi}{2}$ and $\frac{\pi}{2}$, and those of θ, 0 and π.

Hence

$$\frac{\partial^2\mathrm{A}}{\partial x^2}+\frac{\partial^2\mathrm{A}}{\partial y^2}+\frac{\partial^2\mathrm{A}}{\partial z^2}=-2\rho\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}}\int_0^\pi\frac{\sin\theta\,d\theta\,d\phi}{\sqrt{1-\frac{u^2}{c^2}\sin^2\theta}}$$
$$=-2\pi\rho\int_0^\pi\frac{\sin\theta\,d\theta}{\sqrt{1-\frac{u^2}{c^2}\sin^2\theta}}=-\frac{2\pi\rho c}{u}\log\frac{c+u}{c-u}.$$

If in the expression for A we make $x=0$, $y=0$, $z=0$, we get for the value of A at O

$$\frac{\pi\rho a^2c}{u}\log\frac{c+u}{c-u},$$

which vanishes with a, $\frac{\partial^2\mathrm{A}}{\partial t^2}$, having the same linear dimensions as A, also vanishes with a.

It follows, therefore, that

$$\mathrm{A}=\int\frac{dq}{2\pi r\left(1-\frac{u_r}{c}\right)}$$

is the solution of

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = -\rho\frac{c}{u}\log\frac{c+u}{c-u},$$

ρ being the density and u the velocity of the electricity at any point.

If, now, we write

$$A = \int \frac{u\,dq}{2\pi c \log\frac{c+u}{c-u}\left[r\left(1-\frac{u_r}{c}\right)\right]},$$

where u is the velocity that dq had when at its companion point, then

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = 0$$

at any point where there is no electricity, since u is a function of $t-\frac{r}{c}$.

But at any point where there is electricity it satisfies the equation

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = -\rho.$$

If this is not evident it can easily be shown to be true by using the method of the small sphere as before. In this integral u means the velocity of the element dq when at its companion point. The companion point of P coincides with P, and therefore there the actual value of u is the velocity at the companion point.

In like manner

$$A = \int \frac{u\,u_x\,dq}{2\pi c^2 \log\frac{c+u}{c-u}\left[r\left(1-\frac{u_r}{c}\right)\right]}$$

is the solution of

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = -\rho\frac{u_x}{c}.$$

In this latter equation u_x means the x component of the actual velocity at P: in the integral it means the x component of the velocity of dq when at its companion point, which is a function of $t-\frac{r}{c}$. Similar expressions may be written down for the solutions of

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = -\rho\frac{u_y}{c}, \quad \text{and} \quad \nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = -\rho\frac{u_z}{c}.$$

Thus we have determined the scalar potential and the components of the vector potential at P. These expressions being true for every point and for every distribution of moving electricity, it would seem to follow that for a single charge e at Q moving in any manner the scalar potential at any point P is

$$\frac{eu}{2\pi c \log\frac{c+u}{c-u}\left[r\left(1-\frac{u_r}{c}\right)\right]},$$

and the components of vector potential

$$\frac{e\,u\,u_x}{2\pi c^2 \log\frac{c+u}{c-u}\left[r\left(1-\frac{u_r}{c}\right)\right]}, \qquad \frac{e\,u\,u_y}{2\pi c^2 \log\frac{c+u}{c-u}\left[r\left(1-\frac{u_r}{c}\right)\right]},$$

$$\frac{e\,u\,u_z}{2\pi c^2 \log\frac{c+u}{c-u}\left[r\left(1-\frac{u_r}{c}\right)\right]}.$$

If the square of $\frac{u}{c}$ be neglected, we get

$$\frac{e}{4\pi r\left(1-\frac{u_r}{c}\right)}, \qquad \frac{e\,u_x}{4\pi c r\left(1-\frac{u_r}{c}\right)},$$

$$\frac{e\,u_y}{4\pi c r\left(1-\frac{u_r}{c}\right)}, \qquad \frac{e\,u_z}{4\pi c r\left(1-\frac{u_r}{c}\right)}.$$

Though I have some misgivings as to the validity of the last step of the above argument, I think the expressions given have some advantages over those obtained from them by neglecting the square of $\frac{u}{c}$. Take the case of a point charge e in uniform motion in a straight line. If the potential be taken to be

$$\frac{e}{4\pi r\left(1-\frac{u_r}{c}\right)},$$

it will be found that the potential at any point in the line is $\frac{e}{4\pi a}$, where a is the distance of the point from the moving charge. Thus this potential is independent of the velocity; but it would seem that, if the velocity approaches that of light, the potential at any point of the line in front of the particle should tend to zero.

Again, if a sphere be described round the moving charge as centre, and the integral of normal force due to the moving charge be taken over its surface, it will be found that, with the simpler expression for the potential, the value of the integral is $\frac{ec}{2u}\log\frac{c+u}{c-u}$, whereas with the expression given above, it is e, in accordance with Gauss's Theorem.

XII. *Note on Gravitation.* By O. W. Richardson, *F.R.S., Wheatstone Professor of Physics, University of London, King's College. With an Appendix, by* L. Simons, *D.Sc., Lecturer in Physics, University of Capetown* *.

THIS note is mainly a brief account of experiments undertaken to seek a connexion between gravitation and electricity. The line of attack is largely empirical and follows a train of thought developed prior to the current theories of gravitational relativity †. Although no positive results have been obtained it seems desirable that a short account of the experiments should be published, both on account of the importance of the subject and also because the results may set limitations on the possible scope of other gravitational theories. The central idea was that gravitation might be due to a slight modification of the law of force between the positive and negative electrons out of which matter is built up, such modification arising out of the different amounts of energy associated with the respective positive or negative electrons as evidenced by their different masses. This point of view is to a certain extent antipathetic to the relativity theory of gravitation, and its comparative failure may be considered in some degree a success for the latter.

One consequence of the point of view referred to is that the ratio between weight and mass should not be quite the same for different elementary substances. The experiments of Bessel and Eötvös show that this ratio is extraordinarily constant for a number of substances. Nevertheless experiments on this point were commenced by the writer in 1914, were abandoned during the war, and have now been recommenced by Mr. H. H. Potter. The present note does not

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* Communicated by the Author.

† O. W. Richardson, Phys. Rev. vol. xxxi. pp. 610, 709 (1910); 'Electron Theory of Matter,' chap. xxii. (1914).

refer to those experiments which are still uncompleted. As their subject-matter forms the whole basis of gravitational relativity, their importance is obvious apart from the line of attack here considered, and they will be dealt with separately on completion.

One direction in which we might expect to find effects of the kind here contemplated is in the displacement of the spectral lines as between different isotopes. There is of course such a displacement to be expected on Bohr's theory on account of the dynamical effect of the changed mass of the nucleus. There might, however, be an additional effect due to the modification of the field of force arising from the nuclear charge owing to the change in the mass associated with it. As a matter of fact, Aronberg [*] and Merton [†] both find a small displacement for a given line as between uranium lead—ordinary lead—thorium lead. For example, Merton for $\lambda=4058$ Å.U. finds

$$\lambda\,(\text{Ur. lead})-\lambda\,(\text{ord. lead})=0{\cdot}0050\ \text{A}\pm0{\cdot}0007\ \text{A}$$

$$\lambda\,(\text{ord. lead})-\lambda\,(\text{Th. lead})=0{\cdot}0022\ \text{A}\pm0{\cdot}0008\ \text{A}.$$

Whilst these displacements are small they are nevertheless many times larger than the Bohr shift calculated from the dynamical effect of the change in the mass of the nucleus. Merton also finds a displacement as between thallium from pitchblende and ordinary thallium. On the other hand, ordinary lithium (atomic weight 6·94), which has been claimed to be a mixture of isotopes (atomic weight 7 with a small proportion of 6), shows no evidence of the expected duplicity in its spectral lines. However, there is no evidence of the Bohr shift, which should be large in this case; so that the lithium observation does not seem very helpful in this connexion.

There are, of course, other possible causes for the displacement of the spectral lines of isotopes such as, for example, a small variation in the electrostatic field of the nucleus arising from a difference in the configuration of its electronic constituents; but if, for the sake of argument, we assume it arises from a modification of the law of force of the more fundamental kind now under consideration, the connexion between such modification and the change of wave-length may be calculated as follows:—

Using the notation of 'Electron Theory of Matter,' 2nd edn. p. 616, let capital letters denote positive and small

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[*] Astrophys. Journ. vol. xlvii. p. 96 (1918).

[†] Roy. Soc. Proc. A, vol. xcvi. p. 388 (1920).

letters negative charges. For an electron charge e' mass m' revolving round a nucleus containing positive electrons of total charge E and mass M and negative electrons of total charge e and mass m, the force at distance r apart is

$$F = \frac{1}{4\pi r^2}\Big\{ (E+e)e' + a[(E+e)m' + e'(M+m)]$$
$$+ c\left[(E+e)\frac{m'^2}{e'} + e'\left(\frac{M^2}{E} + \frac{m^2}{e}\right)\right] + g(M+m)m'\Big\}.$$

For isotopes $E+e$, e', and m' have the same value but M, m, E, and e are different. The difference in F for two isotopes is thus

$$\delta F = \frac{1}{4\pi r^2}\left\{ ae'\delta(M+m) + ce'\delta\left(\frac{M^2}{E} + \frac{m^2}{e}\right) + gm'\delta(M+m)\right\}.$$

To a first approximation M/E and m/e are respectively constant, being the oxygen nucleus and negative electron values, also m/M is small, so that

$$\delta F = \frac{1}{4\pi r^2} A\delta W,$$

where $A = ae' + ce'\dfrac{M}{E} + gm'$

and $W = M + m.$

The forces will thus be the same as if the nuclear charge were increased by an amount

$$\left(a + \frac{M}{E}c + g\frac{m'}{e'}\right)\delta W \equiv B\delta W.$$

According to Bohr's theory the frequency of any particular spectral line is

$$\nu = 2\pi^2 \frac{M_1 m_1 E_1^2 e_1^2}{(M_1 + m_1)h^3}\left\{\frac{1}{\tau_r^2} - \frac{1}{\tau_s^2}\right\},$$

e_1 and m_1 being the charge and mass of the circulating electron and E_1 and M_1 the charge and mass of the nucleus and electron system about which it circulates. τ_r and τ_s are positive integers and h is Planck's constant. The corresponding frequency for the isotope is

$$\nu' = 2\pi^2 \frac{(M_1 + \delta W)m_1(E_1 + B\delta W)^2 e_1^2}{(M_1 + m_1 + \delta W)h^3}\left\{\frac{1}{\tau_r^2} - \frac{1}{\tau_s^2}\right\}.$$

Thus

$$\frac{\lambda'}{\lambda}=\frac{\nu'}{\nu}=1+\delta\mathrm{W}\left[\frac{m_1}{\mathrm{M}_1(\mathrm{M}_1+m_1)}+2\frac{\mathrm{B}}{\mathrm{E}_1}\right]$$
$$+\delta\mathrm{W}^2\left[\frac{m_1}{\mathrm{M}_1(\mathrm{M}_1+m_1)^2}+2\frac{\mathrm{B}}{\mathrm{E}_1}\frac{m_1}{\mathrm{M}_1(\mathrm{M}_1+m_1)}+\frac{\mathrm{B}^3}{\mathrm{E}_1{}^2}\right]+\ldots,$$

and the relative shift

$$-\frac{\delta\lambda}{\lambda}=\delta\mathrm{W}\left[\frac{m_1}{\mathrm{M}_1(\mathrm{M}_1+m_1)}+2\frac{\mathrm{B}}{\mathrm{E}_1}\right]$$
$$+\delta\mathrm{W}^2\left[\frac{m_1}{\mathrm{M}_1(\mathrm{M}_1+m_1)^2}+2\frac{\mathrm{B}}{\mathrm{E}_1}\frac{m_1}{\mathrm{M}_1(\mathrm{M}_1+m_1)}+\frac{\mathrm{B}^2}{\mathrm{E}_1{}^2}\right]+\ldots$$

The atomic weights of the different leads tested by Merton do not appear to have been measured, but we need not go beyond the order of magnitude of the different terms, and for this accuracy it will be sufficient to put

$$-\delta\lambda/\lambda=1{\cdot}2\times10^{-6},\quad \delta\mathrm{W}=0{\cdot}5,\quad \mathrm{M}_1=207,\quad \frac{1}{m_1}=1860.$$

The first term on the right represents the Bohr shift. It amounts to about 6×10^{-9} and therefore forms only a small fraction of the observed $\delta\lambda/\lambda$. It appears that all the other terms are small except the second which has to account for practically the whole of $\delta\lambda/\lambda$. On the type of view here considered then it appears that B/E_1 must be of the order 10^{-6}.

If B/E_1 were as large as this it would have several notable consequences. In terms of the coefficients the value of B/E_1 is $\frac{1}{\mathrm{E}_1}\left(a+\frac{\mathrm{M}}{\mathrm{E}}c+g\frac{m'}{e'}\right)$. The last term in this expression represents the ordinary Newtonian gravitational force due to the mass m' of the electron. On substituting the numerical data the value of $\frac{gm'}{\mathrm{E}_1e'}$ is found to be $2{\cdot}5\times10^{-16}$. It is thus a very minute fraction of the whole of B/E_1. This would mean that in a gravitational field positive and negative electrons would be acted on by opposite forces of nearly equal magnitude but much larger than the Newtonian forces for neutral particles of equal masses. In an insulator at rest this would give rise to an electric polarization proportional to the gravitational intensity. In a conductor in equilibrium we should expect a separation of the charges giving rise to an equilibrating electric field. In the earth's gravitational field, if $B/E_1 = 10^{-6}$, this field should be equal to $2{\cdot}13 \times 10^{-3}$ volt/cm.

We might also expect currents to be generated in a circuit of which part was falling under gravity relative to the rest. I have made experiments to test this point. About 200 lb. of mercury were allowed to fall in a continuous stream from a container through a short tube 9 mm. in diameter for a distance of about a metre to a container at a lower level. The containers were electrically connected by mercury-filled glass tubes (to avoid thermoelectric disturbances) with a galvanometer having a resistance of 600 ohms and a sensitivity of 1 division for $2{\cdot}6 \times 10^{-10}$ ampere. The resistance of the rest of the circuit was negligible in comparison. No deflexion amounting to a scale-division could be observed when the mercury was running steadily. At the start and finish rather irregular deflexions were observed, but there are a number of ordinary explanations which might account for them. However, I do not consider that these experiments rule out the possibility of such effects at the start and finish. In order to settle this point definitely more elaborate apparatus would be required than I happened to have available.

On the view we are considering the force on an electron in a gravitational field would be quite different from the ordinary Newtonian attraction on its mass. The acceleration of an electron in the earth's gravitational field, for example, would be about 10^{12} cm. sec.$^{-2}$. A correlated effect is that the apparent weight of equal electric charges should, to a very close approximation, change sign with the sign of the charge. (The approximation neglects the gravitational term in B, which is about 10^{-10} of the whole.) This can be tested by placing a very light earth-connected plate in a median position in a flat insulated metal box and finding if the apparent weight of the plate varies with the sign of the charge on the box. Very careful experiments on this principle have been made in the Wheatstone Laboratory by Dr. L. Simons, and as the result is important they are described in the appendix. Dr. Simons finds no displacement, although he concludes that he could have detected a deflexion equal to about one-third of that to be expected if $B = 10^{-6} E_1$.

The charges which would develop on a conducting sphere of gravitating matter are apparently much too small to account for the earth's magnetic field. I find that the equations are solved by an electric distribution of uniform volume density throughout the sphere, and if the sphere is uncharged an equal and opposite total charge of uniform surface density over the surface. If this rotates uniformly in a periodic time τ the magnetic field at external points is the same as that of a small magnet along the axis of rotation having a magnetic moment

$$\mu = \frac{4\pi}{15} \frac{\mathrm{BM}}{c\tau} \mathrm{R}^2,$$

where M is the mass and R the radius of the sphere and c is the velocity of light. Putting $\mathrm{B} = 10^{-6} \mathrm{E}_1$ and the values of M and R for the earth, this gives the magnetic intensity at the pole as $5{\cdot}9 \times 10^{-12}$.

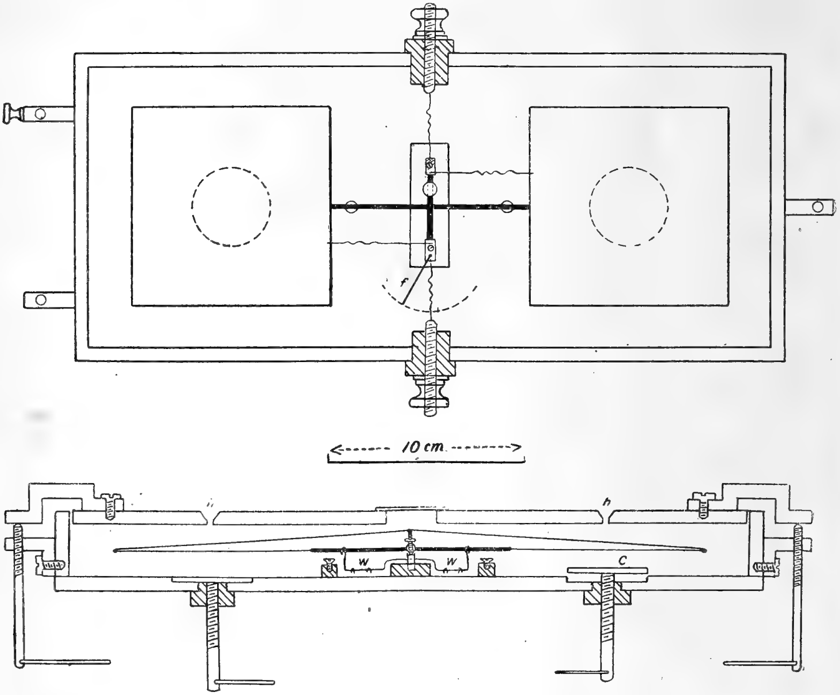
One positive conclusion which may be drawn from these notes is that the displacement of spectral lines as between isotopes cannot be regarded as furnishing evidence of the existence of cross terms in the law of force between electric charges and mass elements. Its explanation is probably to be sought in an electrostatic effect of some variation in the geometrical structure of the elements of the nucleus.

APPENDIX by Dr. L. Simons.

The apparatus consisted of a heavy brass box of internal dimensions $34 \times 14 \times 2{\cdot}5$ cm., the lid, resting on three screws, being adjustable. A silica framework consisting of two squares of 10 cm. side were mounted coplanar with their centres at a distance of 20 cm. apart. and a silica cross-piece arranged to carry brass ferrules at its ends through which there passed pointed steel screws which rested on steel planes. Aluminium foil 0·002 cm. thick was fixed over the two squares, and the whole balanced symmetrically within the box which was lined with the same aluminium in order to avoid irregularities arising from contact e.m.f. The total mass of the moving parts of the balance was approximately 4 gm. The sensibility could be very finely adjusted either by means of the weights (w) or by means of the screw pivots. The motion of the balance could be observed by means of a mirror attached to the cross-bar and a telescope and millimetre scale at a distance of about 1 metre, the adjustment for zero being made with the flag (f), which was a short strand of silica movable by a lever from the outside of the wooden box containing the apparatus. The vanes could be charged from the outside *viâ* thin copper wires joining them to the brass ferrules, thence across the steel pivots to the steel planes on which they rested, which in turn were connected to terminals outside the box.

The sensibility was found directly. A number of small weights were cut from the aluminium foil mentioned above, the mass of each being $2{\cdot}18 \times 10^{-5}$ gm. These could be picked up on a small brush and pushed through the holes (h) directly over the centre of each vane. Independent determinations gave the sensibility to be $1{\cdot}42 \times 10^{-6}$ gm. per millimetre deflexion on the scale, and as this was considerably magnified by the telescope a motion of one-tenth of a division could easily be observed.

Fig. 1.



The method of experimenting was as follows. The lid of the box was first adjusted so that it was approximately parallel to the bottom and at a distance of about 2·6 cm. from it. One vane and the box were kept earthed and the other vane charged to, say, 100 volts ; generally there was a motion of the balance, but by means of the flag the vane to be charged could be adjusted so that it lay practically midway between the top and bottom of the box. On recharging, it was now almost indifferent as to which way it was attracted, up or down. The final adjustment was made by screwing the lid up or down by a small amount. In practice it was found to be quite impossible so to arrange matters that there was equilibrium on charging the vane, but no matter how finely the adjustment was made it was found that the behaviour of the vane at this sensibility was quite independent of the sign of the charge upon it up to a potential of 1000 volts.

It should be mentioned that had any difference in behaviour been observable it was intended to isolate a circular portion (*c*) of the bottom of the box, adjust the opposite vane, as above, for temporary equilibrium when it was charged, say, positively. On switching over to the negative let us suppose that this vane experienced a small downward force, this force could now be counterbalanced by putting a small potential simultaneously on the isolated portion of the bottom of the box. However, as no difference in behaviour between the vane being charged positively or negatively was observed, this portion of the apparatus was not used but was kept screwed down flush with the bottom.

Having regard to the dimensions of the vane and its distance from the top and bottom of the box, the quantity of electricity upon it when charged to 1000 volts was approximately 41 e.s.u. Now a deflexion for a mass of $1 \cdot 5 \times 10^{-7}$ gm. on the centre of a vane could have been observed, and therefore there was no observable difference in the force on ± 41 e.s.u. of charge in the gravitational field greater than $1 \cdot 5 \times 10^{-7} \times 980$ dyne, or in other words there was no observable resultant gravitational electrostatic field greater than approximately $1 \cdot 8 \times 10^{-6}$ dyne/e.s.u.

June 3rd, 1921.

XIII. *Characteristic X-Rays from Boron and Carbon.* *By* A. Ll. Hughes, *D.Sc., Research Professor of Physics, Queen's University, Kingston, Canada* *.

THE purpose of this investigation was to see if some progress could be made towards filling up the gap between the shortest ultra-violet waves hitherto produced and the longest X-ray waves known. The Kα emission-line of sodium, λ 11·8, and the Lα emission-line of zinc, λ 12·3, are the longest wave-lengths which have been identified in the X-ray region. There is no reason to believe that X-rays of still longer wave-length cannot be produced, but no crystal has been found, or is likely to be found, with

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* Communicated by the Author.

spacings between its planes sufficiently large to measure appreciably longer wave-lengths. The spacing available sets an abrupt limit to the study of X-ray spectra in the direction of longer wave-lengths. It is unlikely, therefore, that the spectrum can be extended more than a few Ångström units by the method of crystal analysis. From the ultra-violet end, steady progress has been made in identifying shorter and shorter wave-lengths by Lyman and by Millikan, who used diffraction gratings. The furthest line yet photographed in the ultra-violet spectrum is λ 202 *, a line in the spectrum of nickel (Millikan). In Millikan's work the wave-length of the lines in the extreme ultra-violet is only about one-seventieth of the distance between the rulings on the grating, as contrasted with from one-third to one-sixth when the grating is used in the visible. While there is no factor in the diffraction grating which sets an abrupt limit to the extension of the ultra-violet spectrum, it is evident that the closing of the gap between ultra-violet light and X-rays by a diffraction grating will be attended with increasing difficulties. The gap yet to be explored extends from λ 202 to λ 12.

The principle underlying the method of this research is as follows:—Experiments by Beatty and others have shown that when an element is bombarded by electrons, whose energy is increased by steps, the characteristic radiation is called out when the energy exceeds a certain critical value. This, superposed on the general radiation, causes a more or less abrupt increase in the curve connecting the intensity (measured by ionization) of the radiation with the energy of the electrons impinging on the element. In this work the radiation emitted by carbon (and boron) bombarded by electrons was allowed to fall on a metal plate, and the total photo-electric current leaving it measured as a function of the energy of the impinging electrons. A discontinuity in the slope of the curve was taken to point to the excitation of the characteristic radiation. The wave-length of the radiation is connected with the energy of the electrons by the well-known quantum relation

$$Ve = h\nu = hc/\lambda,$$

where V is the potential accelerating the electrons, e the charge on the electron, h Planck's constant, ν and λ the frequency and wave-length of the radiation, and c the velocity of light. When V is expressed in volts and γ in Ångström units, we have

$$V = 12331/\lambda.$$

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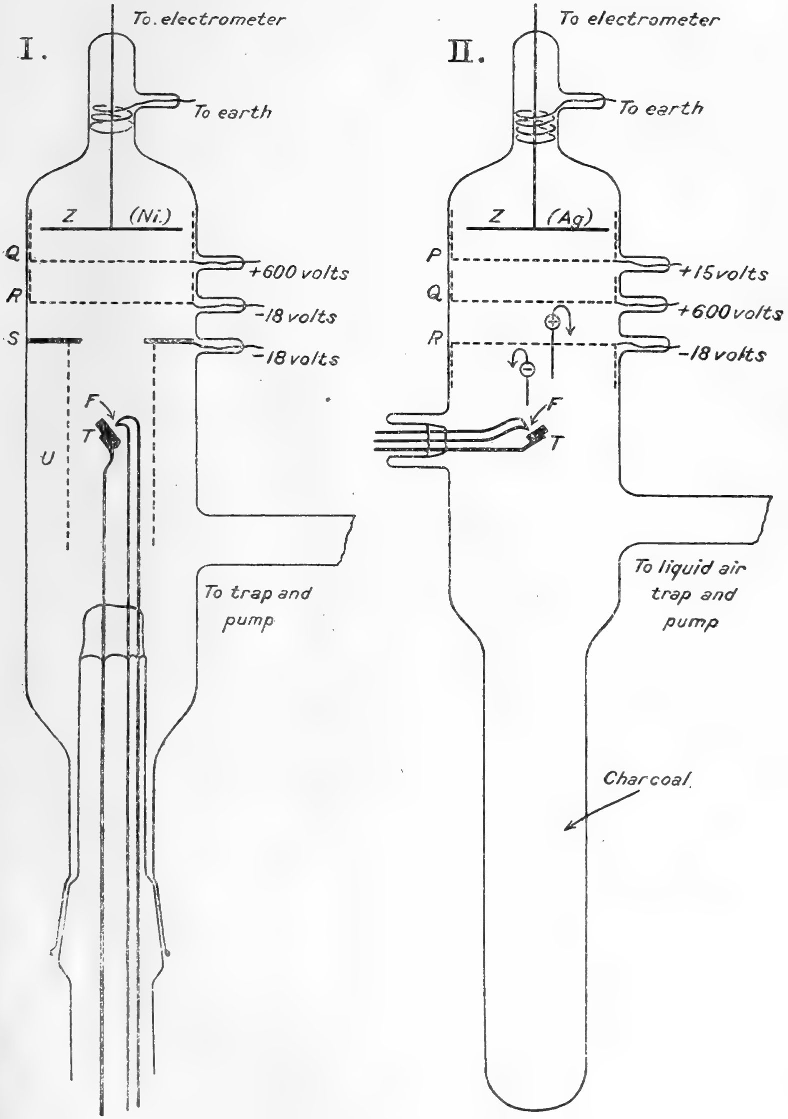
* Millikan, Astrophysical Journal, lii. p. 47 (1920).

Apparatus.

Two slightly different types of apparatus were used in the course of the research. In the first type the tungsten leads

Fig. 1.



carrying the cathode filament, together with the boron target, were mounted in a glass tube which fitted into the main apparatus by means of a ground-glass joint, sealed by De Khotinsky cement. This enabled one easily to change the filament or target. In the second type of apparatus the ground-glass joint was replaced by a sealed glass joint, and a wide tube containing specially prepared charcoal was added, as shown. It was hoped that apparatus II. would give better vacuum conditions. Both pieces of apparatus were made of Corning G 702-P glass, through which tungsten wires were sealed to make connexion with the metallic parts inside. (Owing to the high melting-point of this glass, it can be heated to from 500° to 600° C. during the outgassing process, and its mechanical strength and resistance to sudden cooling are advantageous in a complicated piece of apparatus.)

The radiation was produced by the impact of electrons from a hot tungsten filament F on a carbon or boron target T, 1 mm. away. Part of the radiation fell on the plate Z (nickel in apparatus I. and silver in apparatus II.), which emitted photo-electrons under the action of the radiation. The photo-electric current was measured by the rate of charging-up of an electrometer. The electron current was held constant at a selected value by slight adjustment of the heating current when necessary. The potential accelerating the electrons was measured by a Weston voltmeter (and multiplier when beyond the range).

As the photo-electric current rarely exceeded 10^{-13} amp., and as the electron current from F to T was generally between 10^{-5} and 10^{-3} amp., it was necessary to make sure that the effect measured was really due to the photo-electric effect of the radiation, and not due in some way to electrons or positive ions finding a path upwards. To ensure this, fine gauzes (1 mm. mesh), 20 mm. apart, were fitted into the apparatus, as shown. The field accelerating the electrons from F to T was produced by keeping F at zero potential, while the potential of T was varied from + 5 to + 500 volts. Thus, if the lower gauze R were kept at a negative potential, no electrons could possibly pass upwards from the neighbourhood of the hot cathode and target; but, on the other hand, this arrangement would help positive ions, if any were produced, to pass through the gauze R. To turn these back, the gauze Q was kept at a higher positive potential than any value of the potential ever applied to F. Hence the positive ions, if any came through R, would be turned back towards R. (The effect of the gauze on positive ions and electrons is indicated in apparatus II., fig. 1.) The only way, then, for the metal plate Z to acquire a positive charge would be for the few positive ions turned back on R to release electrons here, and for these electrons, by virtue of R being 18 volts negative to Z, to travel to Z. This, however, would give Z a negative charge. To account for a spurious positive charge simulating the photo-electric effect sought, one would have to assume that each electron hitting Z released more than one electron on impact. The work of v. Baeyer, and still more the recent work of Millikan and Barber [*], shows that these 18-volt electrons could only release a much smaller number of electrons than the original number of 18-volt electrons impinging on Z. According to Millikan and Barber, electrons must have energies of 200 volts or more before the secondary electrons exceed the primary in numbers. This result is for copper; presumably something of the same order holds for nickel and silver. One may safely conclude that the positive current from the plate Z is a pure photo-electric current due to radiation [†].

The boron or carbon target was subjected to a preliminary heat treatment, lasting several hours, in a silica tube heated to redness and exhausted by a diffusion-pump. The tungsten filament, ready mounted in its glass tube, was heated to a white heat in an auxiliary vacuum for some time. The target was mounted 1 mm. away from the filament, and the glass tube carrying the target and filament so assembled was quickly sealed into the main tube, which was then exhausted by a diffusion-pump. An electric oven was built up around the apparatus and heated to 500° C. with the pumps running continuously. After several hours' heating, the pressure fell to about ·00002 mm. The heating was then continued at 380° C., during which treatment no pressure

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[*] Millikan and Barber, Proc. Nat. Acad. Sci. vii. p. 13 (1921).

[†] To get an idea of the effect of allowing positive ions to get through, the potential of Q was reduced to zero. With 45 volts accelerating the electrons from F to T (*i. e.*, F zero, T +45 volts), the positive ion effect plus the radiation effect at Z (Q, zero) was only about four times the radiation effect alone (Q, +600 volts). With higher accelerating voltages the ratio was decreased, as the radiation increased rapidly with the energy of the bombarding electrons. It is unlikely that these positive ions, when turned back on the upper side of R, would release anything like as many electrons as there were positive ions, and, in any case, we have already seen that these 18-volt electrons from R impinging on Z could not account for the flow of electrons from Z. Incidentally, it may be mentioned that when the potential of Q was zero permitting positive ions to get to Z, the positive ion effect was of the order of 10^{-9} of the electron stream from F to T.

could be measured, it certainly being less than ·000001 mm. After the first few hours' initial heating, liquid air was placed around the trap between the pump and apparatus. By the time the temperature had been reduced to room-temperature (the pumps working continuously), one may be confident that the vacuum was very good. (Outgassing at a series of gradually decreasing temperature is said to be particularly effective*.) The whole procedure usually occupied two days. Liquid air was placed around the charcoal tube in apparatus II. two or three hours before observations were made.

In apparatus II. a wide-mesh gauze P was introduced between Q and Z, to increase the steadiness of the electrometer needle. Slight fluctuations in the cells giving the 15 volts had much less inductive effect on Z and the associated electrometer than when Z was faced directly by Q at 600 volts, when the same relative fluctuations in the cells would produce an effect forty times as big.

Experimental Results.

Boron †.—A set of observations obtained with boron on one occasion (using apparatus I.) is shown in fig. 2. Horizontally we have the voltage applied between T and F, measuring the energy of the impinging electrons, and vertically we have the photo-electric current from Z per unit electron current between T and F. It will be seen that as the observations were repeated (a run with decreasing potentials following one with increasing potentials and *vice versâ*), there was a steady increase in the magnitude of the effect. To eliminate the time factor to some extent, the mean of the four runs was found and plotted, as shown in the upper part of the figure. It will be seen that there is an abrupt change in the slope of the curve at 150 volts. On attempting to repeat this some days later, it was found that a practically continuous line, with only a slight break such as that shown in fig. 3, was obtained. Many attempts were made to find out the conditions which gave rise to the type of curve shown in fig. 2. The effects were tried of subjecting the boron to an intense electronic bombardment, of taking it out and grinding a new surface, and of using a newly-fractured unground surface. Only on one other occasion was a set of curves similar to that shown in fig. 2

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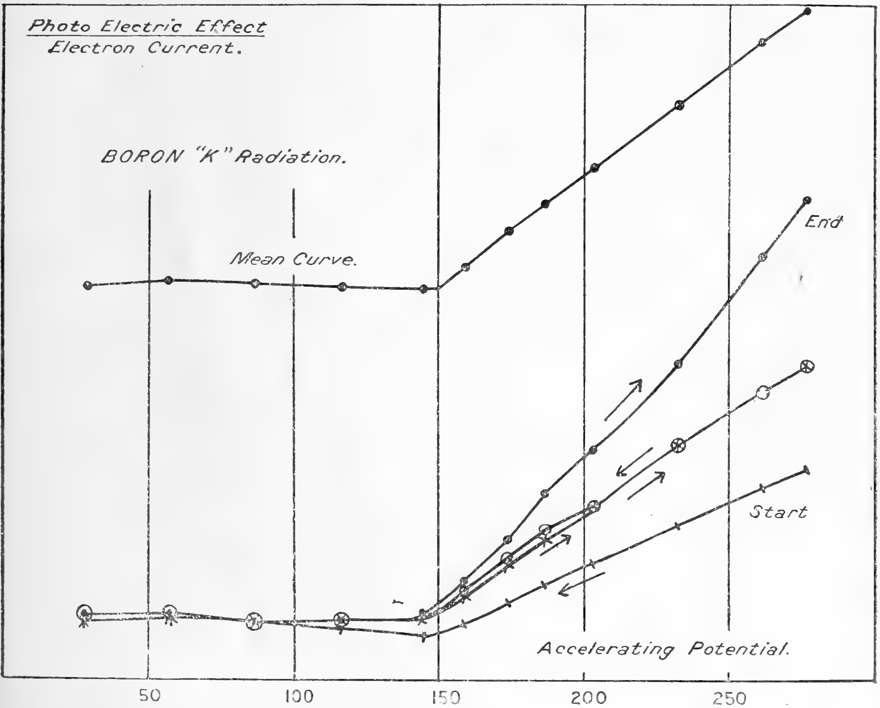
* Dushman, Gen. Elec. Rev. xxiv. p. 251 (1921).

† The author is indebted to Dr. W. R. Whitney, of the General Electric Company, for the boron.

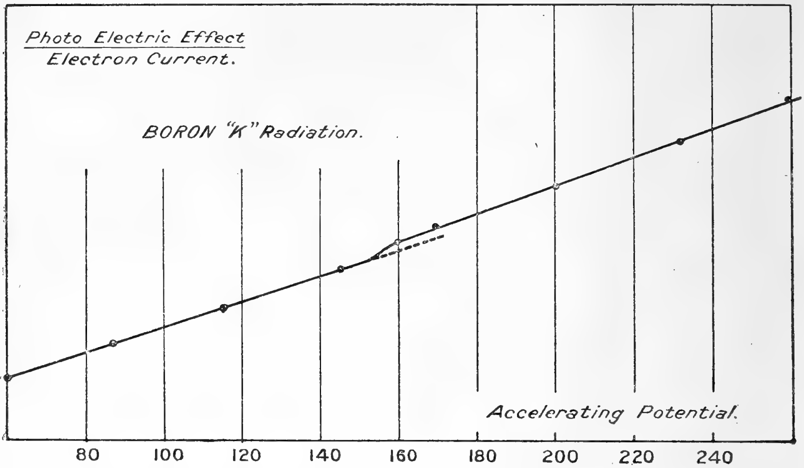
obtained (giving 150 volts as before). It is remarkable, however, that whether the break was but slight, or abrupt, it always appeared in the vicinity of 150 volts. When it was found that conditions which gave rise to the curves in fig. 2 could not be reproduced at will, and that generally curves with slight breaks, *e. g.* fig. 3, were obtained, efforts were concentrated on locating these slight breaks. In view of progressive time-changes (generally smaller than those shown in fig. 2), it was decided to restrict observations to a certain number of selected accelerating potentials, so as to complete a run in a short time (thirty to fifty minutes), and to repeat these runs with increasing and decreasing potentials alternately. (One could have spent the same total time on one run only, but with from four to six times as many points. However, the procedure adopted was considered more satisfactory.) Then, if each run individually showed a definite break, the average of four or six consecutive runs

Fig. 2.



(alternately increasing and decreasing) was found and plotted. In this way slight accidental variations disappeared, while the break showed up distinctly. It is fortunate that the lines above and below the break-point are so nearly straight, otherwise it would have been almost impossible to detect a slight discontinuity in the slope of the curve. Both types of apparatus (I. and II.) were used for boron.

Fig. 3.



Five curves (each the mean of four, six, or eight consecutive runs) were obtained for boron giving breaks at 150, 150, 145, 153, and 145 volts. We may take the mean value to be 148 volts. This is regarded as the energy of the electron necessary to call out the K-radiation of boron, and by the quantum relation it corresponds to a wave-length λ 83·5.

A number of observations were carried out in the region 10 to 40 volts in the hope of locating the L-radiation. Fig. 4 shows the average of six consecutive runs, each showing a break between 24 and 26 volts, the break in the mean curve being at about 24·5 volts. This corresponds to a wave-length λ 505.

Carbon.—Carbon was used in the form of natural graphite, the specimen from which the targets were cut was said to be 99·5 per cent. carbon. Experiments were carried out in the same way as on boron (apparatus II. being used). Typical curves are shown in fig. 5. The breaks which are taken to correspond to the K-radiation of carbon occur in four different curves at 210, 220, 213, 216 volts, giving a mean at 215 volts. This corresponds to a wave-length λ 57·5.

Fig. 4.

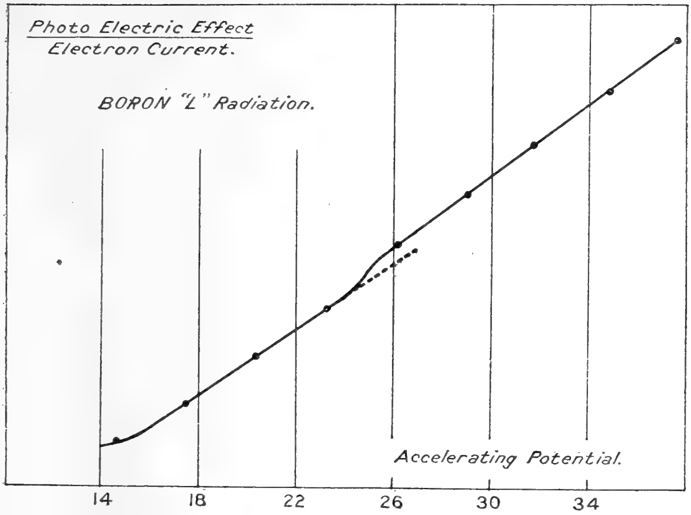


Photo Electric Effect
Electron Current.
BORON "L" Radiation.
Accelerating Potential.
14
18
22
26
30
34

Fig. 5.

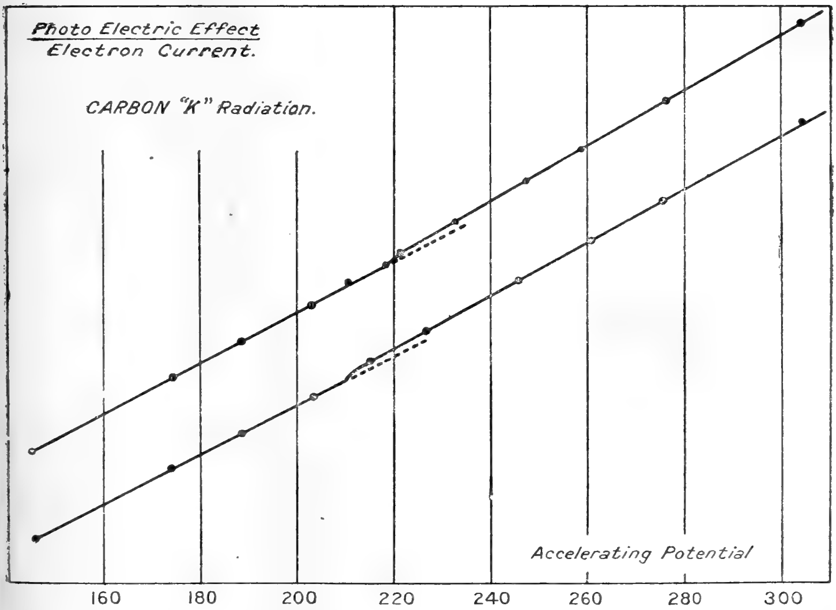
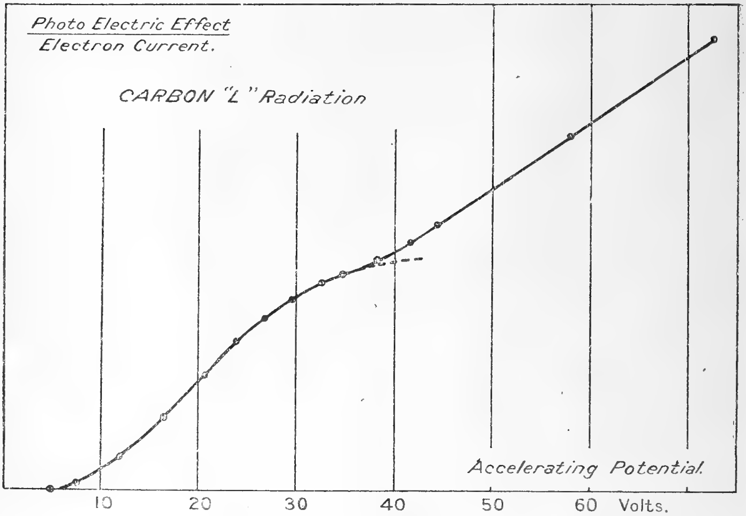


Photo Electric Effect
Electron Current.
CARBON "K" Radiation.
Accelerating Potential
160
180
200
220
240
260
280
300

The character of the curves used in locating the L-radiation for carbon (fig. 6) differs somewhat from that of those obtained for boron. One has to take a point of inflexion rather than a break. This no doubt has to do with the form of the curve for the general radiation in this region, if it could be found apart from any superposed characteristic radiation. The points at which the curvature begins to change to an upward direction, and which are taken to correspond to the L-radiation, are 36·0, 34·0, 34·2, and 35·0 volts, giving a mean at about 34·5 volts. The corresponding wave-length is λ 358.

Fig. 6.



The graphs reproduced in figs. 3 to 6 are chosen partly to illustrate the form of the curves for some distance on either side of the breaks. Several of the values for the breaks were obtained from runs limited to a shorter range of potentials, thus giving points closer together. It is, perhaps, hardly necessary to say that the actual values were obtained from graphs accurately plotted on a large scale.

On many occasions it was found impossible to get curves with a break for either carbon or boron. It was then noticed that this was generally the case after the target had been in use for a long time. On taking the target out and exposing a new surface, either by grinding (boron) or filing (carbon), or by exposing a newly-fractured surface (carbon and boron), the breaks almost always reappeared. Also, when definite breaks were obtained, it was found that time-changes were well marked. With a new surface the photo-electric effect (referred to unit electron current from F to T) was always small, and increased as the experiment progressed to a value perhaps two to four times the initial value. Later on it became much more steady. At first one was tempted to wait till the equilibrium condition had been reached, as measurements seemed then to be more reproducible, but unfortunately, at this stage, the breaks had generally disappeared. It was therefore necessary to take observations as soon as possible after the filament had once been lighted, and then to take observations quickly at equally spaced time-intervals from the highest accelerating potential chosen to the lowest and back again, and repeated several times if possible, so as to obtain data from which a mean curve could be calculated. It is likely that the target got covered with a thin layer of some foreign matter, possibly evaporated tungsten. This would be a plausible explanation of the obliteration of the breaks characteristic of the target, for no doubt a very thin layer would be sufficient to absorb these slow electrons. The increase in the intensity of the radiation as time goes on fits in well with the known fact that the general radiation from heavy atoms is more intense than that from light atoms.

Besides the fact that each curve from which the critical values of the potential are derived is itself a mean of four, six, or eight consecutive runs, *each* run itself showing the break, there is other evidence in favour of the reality of these small but definite breaks. That these breaks are not due in some obscure manner to the particular apparatus and measuring instruments is shown (1) by the fact that both types of apparatus gave breaks at the same place for boron, and (2) that no evidence of the carbon breaks was obtained when boron was used as target, and *vice versâ*. Neither with boron nor with carbon was there any trace of a break between the K and L points, the curve between these points being smooth and very nearly straight.

Discussion.

It is of interest to see how these values for the characteristic radiations of boron and carbon fit in with the values for other elements. The values of the Kα emission-lines are known for the elements down to sodium, while the values of the K critical absorption wave-lengths (Ka) are known to magnesium. The question then arises, which of these shall we extrapolate to compare with our experimental values? The principal radiation emitted by the boron and carbon is no doubt the Kα line; but, if boron and carbon behave like the heavier elements, this radiation cannot be excited unless the quantum of energy in the impinging electron just exceeds that corresponding to the K critical absorption wave-length. As the energy of the impinging electron is the variable in these experiments, it would seem more correct to compare our values with the extrapolated values of the K*a* points rather than the Kα points.

The data are given in Table I. The wave-lengths of the $K\alpha_1$ emission-lines and the K*a* critical absorption wave-lengths are taken from Duane's "Data relating to X-Ray Spectra"*. According to Moseley's law, the square root of the frequency of the X-radiation is almost exactly a linear function of the atomic number of the element. Since, by

TABLE I.

Element.	$K\alpha_1$ emission-line. λ.	V.	$\sqrt{V}$.	K*a* crit. abs. wave-length. λ.	V.	$\sqrt{V}$.	$V_{L\alpha_1} = V_{Ka} - V_{K\alpha_1}$.
Fe (26)...	1·932	6383	79·90	1·740	7087	84·18	704
Cr (24)...	2·285	5396	73·45	2·067	5966	77·24	570
V (23)...	2·498	4936	70·26	2·265	5444	73·78	508
Ti (22)...	2·742	4497	67·06	2·494	4944	70·32	447
Ca (20)...	3·352	3679	60·66	3·063	4026	63·45	347
K (19)...	3·734	3303	57·47	3·434	3590	59·22	287
S (16)...	5·361	2300	47·96	5·012	2460	49·60	160
P (15)...	6·142	2008	44·81	5·758	2142	46·28	134
Si (14)...	7·109	1735	41·65				
Al (13)...	8·319	1482	38·05	7·947	1552	39·40	70
Mg (12)...	9·867	1250	35·35	9·511	1296	36·00	46
Na (11)...	11·88	1038	32·21	11·62	1061	32·58	23
Ne (10)...	14·57	846	29·08	14·5	851	29·17	5
F (9)...	18·32	673	25·95	18·6	664	25·77	neg.
O (8)...	23·67	521	22·82	24·7	500	22·37	„
N (7)...	31·78	388	19·70	34·3	360	18·98	„
C (6)...	44·75	275	16·59	50·7	243	15·59	„
B (5)...	67·7	182	13·48	82·8	149	12·20	„
Be (4)...	114·2	108	10·37	159	77·8	8·82	„
Li (3)...	234	52·8	7·27	417	29·6	5·44	„
He (2)...	585	21·2	4·6	487	25·4	5·05	
H (1)...	1216	10·2	3·2	916	13·5	3·67	

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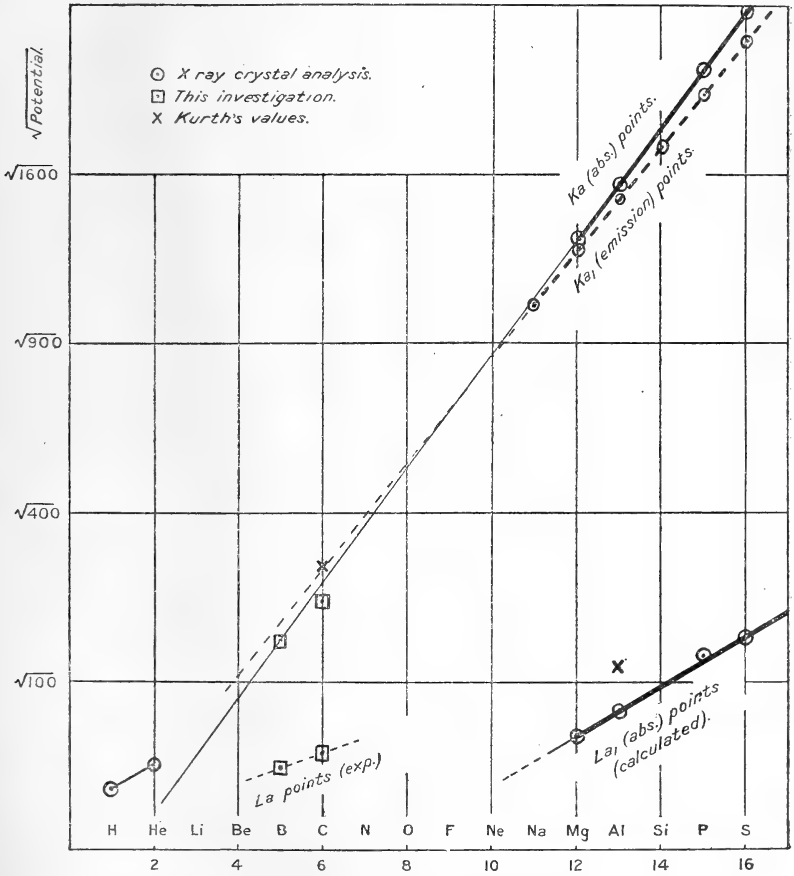
* Duane, 'Bulletin of the National Research Council,' i. p. 383 (1920).

the quantum relation ($Ve = h\nu$) the potential V is proportional to ν, then the square root of the potential should also be almost exactly a linear function of the atomic number. We shall use the potential V in the discussion.

If the relation between $\sqrt{V}$ and the atomic number were strictly linear, then the difference between successive values of $\sqrt{V}$ would be identical. However, they decrease very slightly. For purposes of extrapolation it has been assumed that this slight decrease is regular and holds for elements of atomic number below 11, just as for those above 11. In

Fig. 7.



this way the values for elements from lithium to neon have been calculated. (The departure from the straight line is hardly noticeable in the graph, fig. 7.) The fact that the extrapolated Kα and K*a* lines cross each other between atomic numbers 9 and 10, shows that something has broken down in this region, for it is difficult to conceive of an emission-line being of *shorter* wave-length than the associated critical absorption wave-length. The general trend is to regard the critical absorption wave-length as being the fundamental constant of an X-ray series, and for this reason, and also for the one given earlier, we shall make our comparison with the extrapolated K*a* points. The extrapolated K*a* critical absorption wave-lengths for boron and carbon are 149 volts and 243 volts. Our experimental values are 148 volts and 215 volts.

Kurth [*], in a preliminary note on his work on soft X-rays, states that he finds a definite break in his curves indicating that the K-radiation for carbon occurs at λ 43·6, which corresponds to 283 volts, a value rather more in excess of the extrapolated value 243 than ours is below. The discrepancy between his results for carbon and ours is difficult to understand. No trace of a break near 283 volts (λ 43·6) was noticed in this investigation.

As the K-series is supposed to be the series of shortest wave-length emitted by any normal atom, it is customary to regard the Lyman-series for hydrogen as the K-series for hydrogen. The first line, corresponding to the Kα emission-line (and also to the radiating potential 10·2 volts), has a wave-length λ 1215; while the limit of the series, corresponding to the K*a* critical absorption wave-length (and also to the ionizing potential 13·5 volts), is at λ 912. For helium the radiating and ionizing potentials are 21·2 volts and 25·4 volts, corresponding to λ 585 (recently identified by Lyman) and λ 487. These may be regarded as the Kα emission-line and the K*a* critical absorption wave-length respectively. (The square roots of the values for the ionizing potentials for hydrogen and helium are shown in fig. 7.) It will be seen that they are appreciably off the prolongation of the line passing through the K points for magnesium, aluminium, etc. It is a doubtful matter, however, whether we could expect continuity, seeing that the shell of electrons giving rise to the supposed K-series for hydrogen and helium is so differently situated from the K shell of electrons in other elements. In hydrogen and helium the electrons (one and two respectively) which form the K shell are the only electrons these two elements possess, while in all other elements they are surrounded by one or more exterior shells of electrons. (It is also doubtful whether we should try to

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[*] Kurth, Phys. Rev. xvii. p. 528 (1921).

connect ionizing potentials 13·5 volts and 25·4 volts with the Kα absorption wave-lengths, considering that in the case of these gases the first line of the series under consideration can be called out at the radiating potential. This is, of course, the fundamental difference between the mode of excitation of emission-lines in X-ray spectra and the mode of excitation of the lines of the principal and associated combination series in the ordinary spectra.)

The breaks at 34·5 volts and 24·5 volts for carbon and boron have been associated with the "L"-radiation from these elements. Fortunately the recent work of Millikan[*] enables a check to be made in the case of carbon. Millikan found that the ultra-violet spectrum of carbon vapour stops suddenly at λ 360·5, this being the shortest line of a small group of lines separated from, and further in the ultra-violet than, any other group of lines. The lines in this group are λ 386·4, λ 384·4, λ 372·1, and λ 360·5, and may be regarded, according to Millikan, as the $L\alpha_3$, $L\alpha_{1\,2}$, $L\beta$, and $L\gamma$ lines in X-ray terminology. It is very significant that our experimental value for the potential corresponding to the L critical absorption wave-length is 34·5 volts, giving a value of λ 358, which is just shorter than the wave-length (λ 360·5) of the $L\gamma$ emission-line. Now, although in the ordinary X-ray region there are three critical absorption wave-lengths in the L-series, the La_1 is the most marked and has a wave-length slightly shorter than that of the $L\gamma$ emission-line. Thus our experimental result, combined with Millikan's measurements, fits in well with the general relation. Unfortunately no information as to the extreme ultra-violet spectrum of boron is available to compare with our value, 24·5 volts (λ 505). If this result be correct, boron should show no emission-lines whatever between about λ 505 (the L critical absorption wave-length) and λ 83·7 (the K-series). Millikan considered it possible that in solid carbon the generation of the L-ring rays might altogether be prevented, as the four electrons which form the second (L) ring in carbon "may form a portion of the space lattice structure." The result of this investigation, however, shows that even in solid carbon the L-rays can be excited. As the L shell of electrons in carbon is the outermost shell, it seems quite likely that its state would be affected to some extent by the presence or absence of neighbouring atoms; and we might reasonably expect a difference, perhaps very small, between the type and wave-length of the L emission-lines from gaseous carbon, as in Millikan's experiments, and the

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[*] Millikan, Astrophysical Journal, lii. p. 47 (1920).

type and wave-length of those from solid carbon as generated in these experiments. It would be exceedingly interesting, therefore, to apply Millikan's method (which is susceptible of much greater precision than the method of this work) to the measurement of the L emission-lines for solid carbon. That all X-ray phenomena hitherto investigated are independent of chemical combination and state of aggregation, may well be due to the fact that the phenomena in question have always been associated with internal shells of electrons of the element under consideration, and never with the outermost shell. In fact, we may expect the wave-length of the X-rays associated with the outer shell of electrons to be in the region $\lambda\,500-\lambda\,100$, a region which has yet to be explored.

According to Duane [*], there is an accurate relation between the frequencies of the $K\alpha$ emission-line and the Ka and La_1 critical absorption wave-lengths, which, expressed in volts, is as follows:

$$V_{La_1}=V_{Ka}-V_{K\alpha_1}.$$

Knowing the $K\alpha_1$ emission-line and the Ka critical absorption wave-length, it is possible to predict the La_1 critical absorption wave-length. This has been done in the last column of Table I. and in fig. 7 (assuming that the relation holds for the light elements as for the heavier). Kurth's experimental values for iron and aluminium are 760 volts and 120 volts, which are considerably in excess of the calculated values 704 volts and 70 volts. (Possibly the relation does not hold accurately when the L shell has but few electrons exterior to it.) If we were to apply the above relation to the calculation of the $K\alpha_1$ line of carbon we should get $V_{K\alpha_2}=215-34\cdot5=180$ volts, implying a relative "span" for the K-series of carbon about 50 per cent. greater than for the K-series for elements further down in the periodic table.

Kossel [†] has discussed from a theoretical standpoint the probable course of the K- and L-series for the light elements. He conjectures that, proceeding from the heavier elements to the lighter, the curve joining the L points should be almost a straight line down to neon (10), and that the L-radiation of neon should simply be that associated with its ionizing potential 16 volts. At neon (now that the L shell is outermost and exposed) the curve takes an abrupt

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[*] Duane, 'Bulletin of the National Research Council,' i. p. 383 (1920).

[†] Kossel, *Zeits. f. Phys.* iii. p. 470 (1920).

turn and flattens out, falling but slowly to the point for lithium, which, according to Kossel, is simply the ionizing potential (5·4 volts). Our experimental values for carbon and boron, however, would seem to be considerably above the conjectured line of L points. We also saw that Kurth's values for iron (26) and particularly aluminium (13) were considerably above the calculated line of L points. Further discussion of Kossel's interesting point of view will be postponed until data as to other elements are available. A glance at fig. 7 makes it very clear that more experimental determinations of the K and L points for light elements are much to be desired. Until some method comparable in accuracy with the diffraction grating, or the crystal grating, applicable to the measurement of wave-length between λ 200 and λ 12 is developed, we shall no doubt have to infer the wave-length from potential measurements similar in character to those of the investigation.

Summary.

The photo-electric effect of the radiation from carbon and boron bombarded by electrons has been measured as a function of the energy of the electrons. Two slight but definite breaks in the curves for both carbon and boron were obtained. These are considered to correspond to the K- and L-absorption wave-lengths. The breaks occur at 215 volts (λ 57·5) and 34·5 volts (λ 358) for carbon, and at 148 volts (λ 83·5) and 24·5 volts (λ 505) for boron. The L point for carbon is in good agreement with the values measured recently by Millikan for the L emission-lines of carbon vapour. The K points for carbon and boron are approximately where they would be expected on extrapolating the known values of the Kα critical absorption wave-lengths for elements heavier than magnesium.

The author wishes to express his thanks to Mr. R. A. Lyon for his assistance during part of this investigation.

Queen's University,
Kingston, Canada.
July 1921.

XIV. *The Effect of Gases on the Contact Difference of Potential between Metals at Different Temperatures.*

By O. W. Richardson, *F.R.S., Wheatstone Professor of Physics, and* F. S. Robertson, *M.I.E.E., Lecturer in Electrical Engineering, University of London, King's College* *.

THE present paper deals with some observations of the curves connecting thermionic electron current and applied potential difference (characteristic curves) for the case of a straight hot wire and a coaxal metal cylinder when small known pressures of gases, principally hydrogen, are present. The currents dealt with were rather small, being of the order 7×10^{-8} amp., and approximate saturation was attained under the experimental conditions with accelerating potentials of the order of a volt. Attention has been directed chiefly to the region in which the curves approach the voltage axis. In this region the shapes of the curves are determined by the distribution of velocity among the emitted electrons, by the geometry of the electrodes and the fall of potential down the hot wire. Whilst these factors were not exactly identical in all the comparative experiments, it is believed that the effects of variation in them are practically negligible, with the result that the shapes of the different curves under comparison are invariable. This is true, as may be seen from the diagrams, figs. 2, 4, and 5, not only for the curves taken under high vacuum conditions, but also for those taken when small quantities of hydrogen were admitted.

Whilst in general the curves are of the same shape they are not in identical positions, but those obtained in the presence of hydrogen are displaced along the voltage axis as compared with those obtained in a vacuum. Inasmuch as for a given maximum or saturation current the shapes of the curves are the same, it is reasonable to infer that the infra-saturation currents will be sensibly the same function of the true voltage between the electrodes. Now the voltage plotted in the diagrams is the voltage between the central point of the hot wire and the surrounding cylinder as read on a voltmeter which in effect is inserted between these points. This differs from the true voltage by an amount equal to the contact difference of potential between the surfaces plus an effect arising from the drop of potential due to the heating current down the wire. With the arrangements used the last effect is believed to have been sensibly the same in all the experiments; so that the displacement of the curves along the voltage axis should be a measure of the change which took place in the contact potential difference between the hot

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* Communicated by the Authors.

wire and the surrounding cylinder under the conditions investigated.

Little need be said of the actual experimental arrangements, which were not for the most part of a novel character in thermionic work. For the production and maintenance of a high vacuum a mercury vapour pump backed by an oil box pump in series with a Geryck piston pump was used, and this could be supplemented when desirable or convenient by a liquid air cooled charcoal attachment. The tubes were mounted so that a vacuum furnace * could be placed over them when desired, so as to get the gas out of the tube walls and electrodes. When desired pure hydrogen could be admitted by gently heating an attached palladium tube with a Bunsen burner and the pressure read off on a McLeod gauge. The pressures of hydrogen used were all so small that they did not affect the shapes of the curves to any ascertainable extent by interference of the gas molecules with the motions of the electrons.

The simplest conditions with a view to the theoretical interpretation of the results would be obtained from the displacements of the curves for the emitting wire maintained at a constant temperature in the different experiments. This, however, involves a good many practical difficulties under the experimental conditions. The problem of maintaining a wire accurately at a constant temperature in presence of varying amounts of gas is one of great difficulty. In the case of platinum for example the effect of absorbed hydrogen on the resistance and the cooling effect of the hydrogen atmosphere vitiate the resistance method of holding the temperature constant. It is doubtful whether the methods of optical pyrometry as applied to thin filaments are sensitive enough for this purpose. Another difficulty arises from the very considerable effect of hydrogen in changing the emission constants of the metal. If a standard temperature is set up for some particular pressure, it may be that on changing to another pressure the emission will be so high that the shape of the characteristics is changed owing to the effect of the self-repulsion of the electrons or, on the other hand, it may be so low that the instruments available are not sensitive enough to make measurements of it. The last is hardly an insuperable objection as it may be overcome by changing over to more sensitive instruments ; but such changing over involves much time at the best, and rapidity of operation is probably the most important factor contributing to success in experiments of this kind.

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* Richardson, 'Emission of Electricity from Hot Bodies,' p. 15.

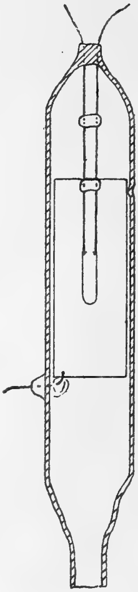
Mainly for these reasons the procedure adopted in all cases has been, after each change in the conditions, so to regulate the temperature of the wire that the saturation current was maintained at approximately its original value. This could be done rapidly by means of a regulating rheostat. Whilst these conditions are not theoretically ideal they are at any rate pretty definite, and are probably the best that could be adopted for a fairly rapid preliminary examination of the phenomena. In many cases a sufficiently close idea of the actual temperature of the wire can be got from its dimensions and from knowledge already available as to the relation between emission and temperature under the given conditions. It is, however, important to remember that the comparisons made in this work are not between wires maintained at a given temperature with different gas pressures, but between wires at such various temperatures as will maintain the thermionic current constant. These various temperatures are in general a function both of the original high vacuum temperature and of the pressure of the admitted gas.

EXPERIMENTS WITH PLATINUM.

The experiments with this metal were made with the tube shown in section in fig. 1. The hot platinum wire was 3·0 cm. long and 0·184 mm. diameter. The leads were of platinum 14·6 cm. long and 0·52 mm. diameter.

The cylinder was of platinum foil and was 5·0 cm. long and 1·88 cm diameter. The tube was cleaned by boiling nitric acid and distilled water before the experiments.

Fig. 1.



In the initial experiments the tube was only exhausted cold and with the wire glowing and was not baked out in the vacuum furnace. This was done so as to realise the conditions referred to in the old experiments on the electron emission from platinum as those pertaining to a new wire*. Under these circumstances the characteristics were found to be fairly sensitive to small quantities of hydrogen. The admission of the hydrogen displaced the characteristics away from the direction of accelerating voltages, indicating that the hot wire had become relatively electronegative with

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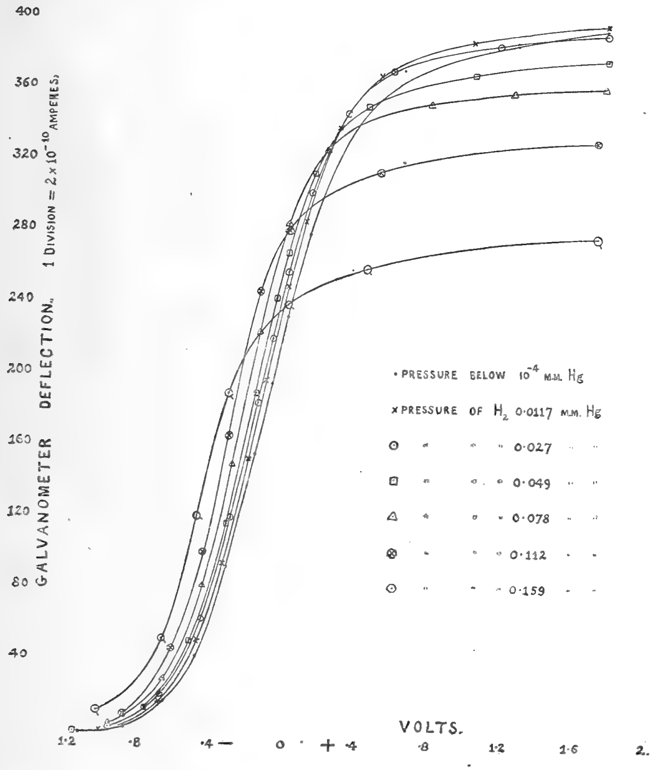
* *Cf.* 'Emission of Electricity from Hot Bodies,' Chap. iv. p. 102.

respect to the cylinder. Initially this displacement appeared to be quite reversible. Thus in a particular test starting with a pressure of 10^{-4} mm. or less, the admission of 0·201 mm. of hydrogen displaced the curve ·35 volt to the left, on pumping the hydrogen out it moved back ·33 volt (*i. e.* to within 0·02 volt of its original position). A typical set of curves obtained after a few hours heating is shown in fig. 2.

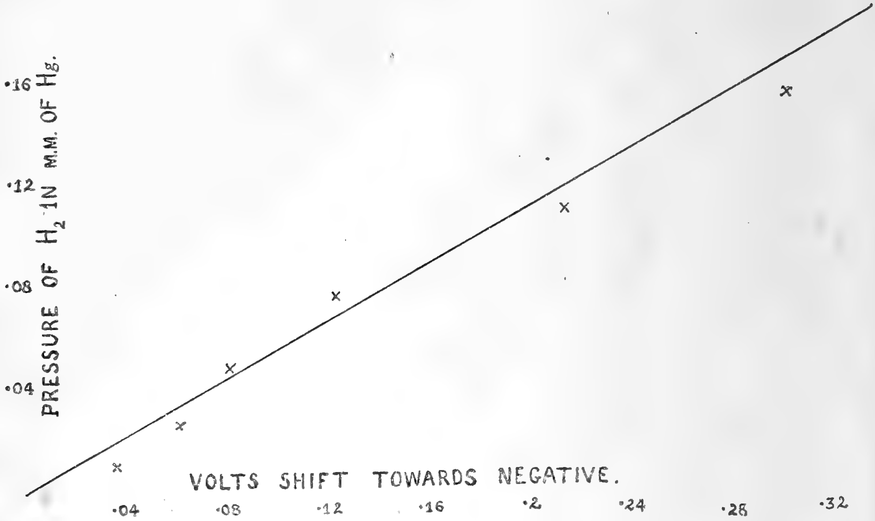
Fig. 2.



The temperature for the high vacuum curve in this case was about 1460° K. The gas pressures at which the various curves were taken are marked on the figure. The displacements are very nearly proportional to the pressure of the admitted hydrogen, as is shown in the plot fig. 3.

After heating for some time the curves became somewhat less sensitive to the admission of hydrogen, and this condition persisted after the tube had been baked out in the furnace and re-exhausted. Typical curves at this stage under different pressures are shown in figs. 4 and 5. Although the displacements are small a careful examination of all the data strongly suggests that they are real. The position of the point on the voltage axis for which the current had half the saturation value is given for a series of pressures in the following table :—

Fig. 3.

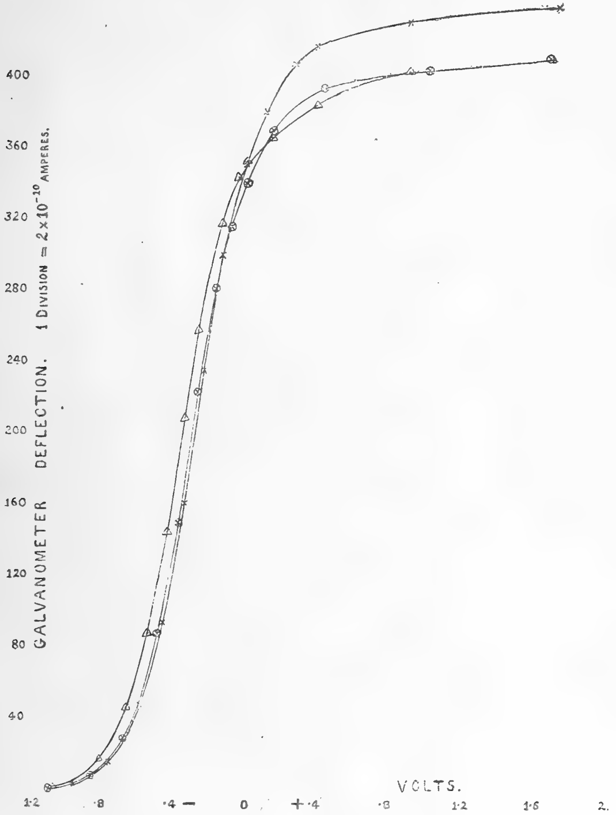


Pressure (mm. × 10^4)	$\ngtr 1$	17	65	463	1000
Voltage for half value......	−·25	−·30	−·35	−·41	−·45

It will be seen that the voltage displacements for a given increment in pressure are greater when the pressure is low. This condition, of which figs. 4 and 5 are typical examples, appeared to be stable and persisted to the end of the experiments, in the course of which the wire was heated some hundreds of hours. The displacements on reducing the pressure were generally somewhat smaller than those obtained when the pressure was increased between the same limits.

This is probably due to the time required to attain equilibrium between the gas and the metal.

Fig. 4.



THEORY OF THE PLATINUM DISPLACEMENTS.

Whilst a complete test of the theory of these effects will require a more elaborate experimental investigation than the present, the results are in some respects definite enough to merit a theoretical discussion on broad lines. A theory of the connexion between contact electromotive force and electron emission from contaminated surfaces has been developed by one of the authors *, and is discussed in connexion with H. A. Wilson's theories of the effect of hydrogen on the

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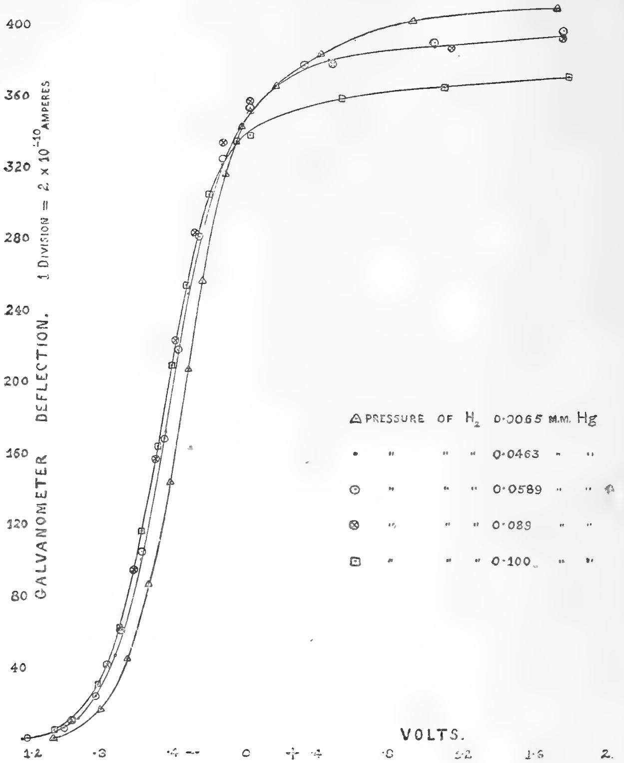
* Richardson, Roy. Soc. Proc. A, vol. xci. p. 524 (1915).

emission from platinum in the 'Emission of Electricity from Hot Bodies,' Chap. iv. pp. 108 *et seq.*, to which the following

Fig. 5.



references relate. In general (equation 34′ p. 109), the contact potential difference between *any* two surfaces at temperature T_1 is

$$V_1 = \frac{kT_1}{e}\log\frac{n}{n'} = \frac{kT_1}{e}\log\frac{i}{i'}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where i and i' are the saturation currents per unit area of the two surfaces at T_1. If the dashed variables refer to the clean metal and the undashed to the metal in presence of gas, it follows from (13) p. 112 that

$$i/i' = (1+ap^c)^{\left(\frac{\alpha}{cT_1}-1\right)}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence

$$V_1 = \frac{kT_1}{e}\left(\frac{\alpha}{cT_1}-1\right)\log(1+ap^c). \quad . \quad . \quad . \quad . \quad (3)$$

For platinum when it is sensitive to hydrogen the constants a, c, and α have the values $a=1\cdot27\times10^4$, $c=0\cdot73$, and $\alpha=2\cdot43\times10^3$ when p is in millimetres of mercury.

The contact potential which is operative during the experiments is not V_1, which refers to a gap between two metal surfaces both at temperature T_1 when one is in a gas-free space and the other in hydrogen at pressure p, but it is the potential difference between two surfaces at temperatures T_1 (that of the hot wire) and T_0 (that of the cold cylinder), both in an atmosphere of hydrogen at pressure p. Let us call this potential difference Ω. To find the value of Ω consider the gap between two blocks of the metal, one maintained at temperature T_1 and the other at T_0, both immersed in hydrogen at pressure p and connected together by a platinum wire. Next consider the work done in taking an electron round a closed circuit starting inside the metal at T_1, across the boundary of T_1, across the gap, then across the boundary of T_0, and finally down the wire to the starting point. This consists of the algebraic sums of the amounts of work done in crossing five surfaces, viz. that between the pure and contaminated metal at T_1 (η_1), that between the contaminated metal at T_1 and the gas (ϕ_1), that across the gap ($-e\Omega$), that from the gas to the contaminated metal at T_0 (ϕ_0), and that between the pure and contaminated metal at T_0 (η_0). Thus by the energy principle

$$e\Omega=\phi_1+\eta_1-(\phi_0+\eta_0). \quad \dots \quad (4)$$

The notation is the same as that in 'Emission of Electricity etc.' p. 109. In the same notation (p. 109 equation 34′) we have

$$eV_1=\phi_1'+\eta_1'-(\phi_1+\eta_1), \quad \dots \quad (5)$$

and similarly

$$eV_0=\phi_0'+\eta_0'-(\phi_0+\eta_0). \quad \dots \quad (6)$$

Now $\eta_1'=\eta_0'=0$; so that

$$e\Omega=e(V_0-V_1)+\phi_1'-\phi_0'. \quad \dots \quad (7)$$

Now, from *loc. cit.* p. 33 equation (16) (equation (15) p. 32 is more accurate but the difference is hardly material)

$$\phi_1'-\phi_0'=\tfrac{3}{2}k(T_1-T_0), \quad \dots \quad (16)$$

and substituting for V_0 and V_1 from (3) above and the similar equation for V_0

$$\Omega=\frac{k}{e}(T_1-T_0)\left\{\frac{3}{2}+\log(1+ap^c)\right\}, \quad \dots \quad (17)$$

or, a little more accurately,

$$\Omega=\frac{k}{e}(T_1-T_0)\left\{\frac{3}{2}+\log(1+ap^c)\right\}-\int_{T_0}^{T_1}\sigma dT. \quad (18)$$

Now we have seen (p. 164, *ante*) that T_1 varied in the different comparative experiments, being a function of the temperature T_2 of the hot wire in the high vacuum experiments and the pressure p of the gas. It was in fact the temperature which at the pressure p gave the emission its high vacuum value and is therefore determined by the equation

$$AT_1^{\frac{1}{2}}e^{-b/T_1}=A'T_2^{\frac{1}{2}}e^{-b'/T_2}. \quad . \quad . \quad . \quad . \quad (19)$$

In this equation the factors $T_1^{\frac{1}{2}}$ and $T_2^{\frac{1}{2}}$ can be treated with sufficient exactness as equal ; so that to such approximation as we require

$$T_1=\frac{b}{b'+T_2\log A/A'}T_2, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and using equations equivalent to *loc. cit.* p. 112 (15) and (17),

$$T_1=\frac{b'-\frac{\alpha}{c}\log\left(1+ap^c\right)}{b'-T_2\log\left(1+ap^c\right)}T_2, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

and the operative contact potential in volts is

$$\frac{V}{300}=\left\{\frac{b'-\frac{\alpha}{c}\log\left(1+ap^c\right)}{b'-T_2\log\left(1+ap^c\right)}T_2-T_0\right\}$$
$$\times\left\{\frac{k}{e}\left(\frac{3}{2}+\log\left(1+ap^c\right)\right)\right\}-\int_{T_0}^{T_1}\sigma dT. \quad (22)$$

Equations (21) and (22) express V as a function of the temperature T_2 of the hot wire in the high vacuum experiments, T_0 that of the cold electrode, the pressure p of the hydrogen, the universal constants k and e, the constants α, c, and a defined already, the emission constant b' for the metal in a vacuum, and the specific heat of electricity σ in platinum. The term in σ is unimportant, but is added for the sake of completeness.

If this theory is correct the observed displacements of the curves will be equal to the differences in the values of V, for a given value of T_2, corresponding to the gas pressures used. Neglecting the unimportant term in σ and substituting the known values of the constants, the values of V given by equation (22) are :—

For $T_2=1200°$ K : when $p=0·112$ mm. $V=0·452$ volt, and
when $p=0·0013$ mm. $V=0·374$ volt.

The displacement for this limit of pressure would thus be $\delta V = \cdot 078$ volt.

For $T_2 = 1460°$ K: when $p = 0\cdot 112$ mm. $V = 0\cdot 629$ volt, and
when $p = 0\cdot 0013$ mm. $V = 0\cdot 504$ volt.

For this value of T_2, $\delta V = 0\cdot 125$ volt.

The experimental value of the displacement over this range of pressure for $T_2 = 1460°$ K. was 0·16 volt; so that the observed effect is in fair accordance with the theory. It should also be added that it is in the prescribed direction.

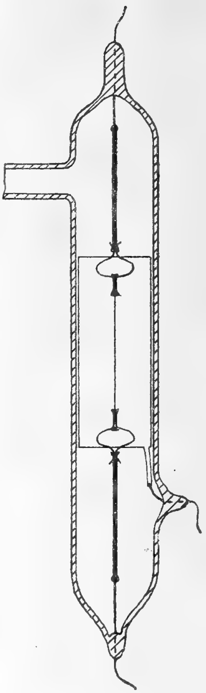
There is one point in this discussion which perhaps has not received sufficient emphasis, namely, that it appears vital in order to reconcile the results with the type of theory dealt with to assume that the hydrogen is in equilibrium not merely with the surface of the hot platinum wire but with that of the cold platinum foil as well. If the hydrogen did not modify the cold platinum surface this would act as a reference surface of constant potential, and a calculation along similar lines for this case shows that the effects should be considerably greater than those observed and in the opposite direction. This is in accordance with the requirement that the hydrogenated platinum surface should be electropositive to a clean platinum surface at all temperatures. The physical reason for the opposite direction of the effect as given by the experiments and supported by the calculations, lies in the fact that the temperature coefficient of the electron work function is negative at all pressures and increases with the pressure of the hydrogen.

EXPERIMENTS WITH TUNGSTEN.

We have made a large number of experiments with tungsten filaments using the type of tube shown in fig. 6. The anodes were of copper foil and were 5·0 cm. long and 1·9 cm. in diameter. The tungsten filaments were 3·0 cm. long and 0·127 mm. in diameter except in the data shown in fig. 7 where the diameter was 0·076 mm. The saturation currents were of the same order as before, 10^{-7} amp. The wires were kept taut along the axis of the cylinder by means of the molybdenum wire springs shown at the ends. These were under slight tension and took up the slack due to expansion on heating.

For some reason we have found it more difficult to get consistent results with tungsten than with platinum. This may be due partly to inexperience in controlling the conditions as the tungsten experiments were, in point of fact, made first. It is probable, however, that the main factor in this is the superior chemical activity of tungsten and copper as compared with platinum. Another difficulty arises from the very marked "clean up" effects with tungsten, which for example when working with hydrogen cause the pressure of the gas to vary considerably in a single experiment. It would take too much space to discuss the whole mass of data which have been obtained in detail, and we shall merely point out the more important conclusions which follow from the experiments.

Fig. 6.



The first point tested was as to whether this admission of small amounts of mercury vapour at a pressure of the order ·001 mm. would displace the curves along the voltage axis. No displacement was observable, indicating that mercury vapour does not affect the contact potential between hot tungsten and cold copper. This is in agreement with the observation * that the electron emission from tungsten is not affected by mercury vapour. In these experiments the mercury vapour was only admitted for short intervals. No doubt if enough were admitted to amalgamate the surface of the cold electrode some displacements would be anticipated.

The problem of the effect of hydrogen was attacked in a similar way to that in the case of platinum. The experiments show that any genuine effect of small quantities of hydrogen is small, and we have not been able to convince ourselves that there is such an effect. The most complete set of data gave the following values for the potentials V on the voltage axis at which the currents had attained half the saturation value at the pressures stated :—

p (mm.)→	·1795	·1745	·1452	·132	·1275	·123	·0855	·078	·075	·0722
V (volts.)→	−1·38	−1·37	−1·32	−1·41	−1·42	−1·45	−1·41	−1·40	−1·43	−1·43

					Means.			
p (mm.)→	·0155	·0085	·00625	·0035	·177	·132	·0777	·008
V (volts)→	−1·57	−1·51	−1·51	−1·46	−1·375	−1·40	−1·42	−1·51

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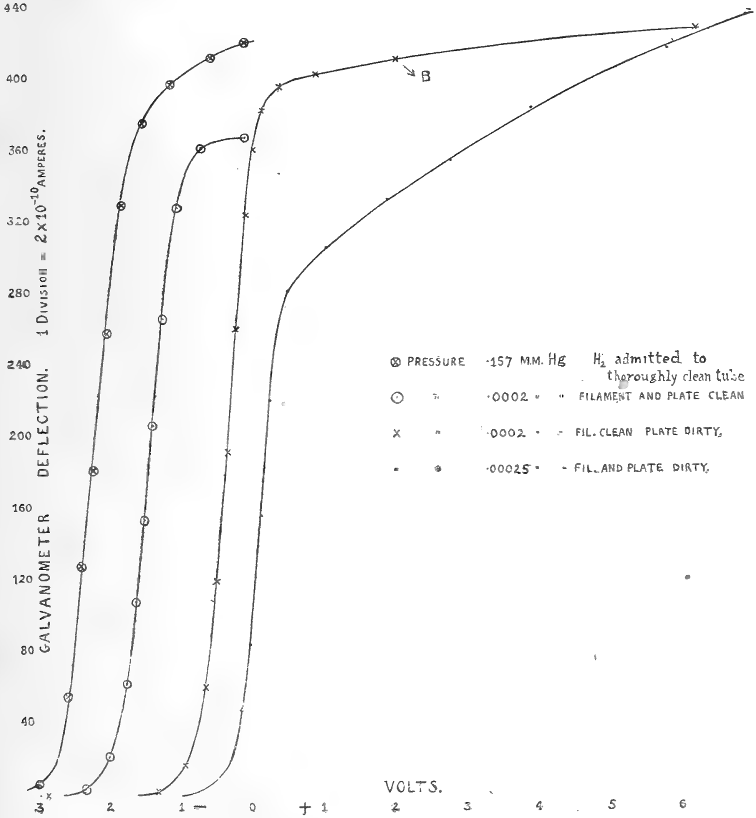
* Richardson, Phil. Mag. vol. xxvi. p. 347 (1913).

These figures suggest that if the effect is real it is in the opposite direction to that observed with platinum, *i.e.* the hydrogen tends to make the hot tungsten more electro-positive with reference to the cold electrode. However, further tests were inconclusive, the gas sometimes apparently causing a small displacement in one direction and at other times in another. All that we are prepared to state definitely at present is that there is no effect of an order of magnitude exceeding that indicated by the figures given above.

Fig. 7.



From time to time, and generally after the apparatus had undergone some drastic treatment, displacements in the characteristics of an entirely different order of magnitude were observed. It seems fairly certain that these large effects are due to contaminations, chiefly by oxidation, of the surfaces of the tungsten filament and the copper anode. The extreme variations which have been observed for the position of the voltage at which the current attained half the saturation value are −2·11 and +0·17; the corresponding curves are shown in fig. 7. This corresponds to a total change in the contact potential difference of 2·28 volts. The extreme displacements in the positive direction along the voltage axis, such as that with the half saturation value at +·17 in fig. 7, were obtained when the tube had been well baked out and the tungsten filament had been intentionally oxidized by glowing in air at a low pressure with the tube cold before testing. The evidence seems clear that an oxidized filament is electropositive by about 0·6 volt as compared with a clean filament at these temperatures.

When the filaments were oxidized the currents were found to be difficult to saturate. This is shown by the upward slope of the relatively flat part of the curve on the right in fig. 7. There seems to be no doubt that this upward slope is due to the oxidized conditions of the tungsten surface. On glowing out the tungsten at a high temperature so as to cause the layer of oxide to evaporate, curves such as B fig. 7 were obtained. These are displaced about 0·6 volt to the left, corresponding to the more electronegative character of the clean tungsten, and at the same time the upward slope of the saturation part is found gradually to disappear.

XV. *On the significance of Einstein's Gravitational Equations in terms of the Curvature of the World.* *By* A. S. Eddington, *M.A., F.R.S., Plumian Professor of Astronomy in the University of Cambridge* [*].

IN the Appendix to the paper on "The Relativity of Field and Matter" [†], I gave a proof of the theorem that Einstein's equations $G_{\mu\nu}=\lambda g_{\mu\nu}$ express the condition that the radius of curvature of sections of the world is the same at all points and for all directions. I have since found that this proof is not sufficiently general. I took too limited a view of the vagaries of which a four-dimensional surface is capable when it has six extra dimensions to twist about in. I assumed that, although ten dimensions of Euclidean space are necessary for the representation of a four-dimensional Riemannian space, a small portion of the latter near the

[*] Communicated by the Author.

[†] Phil. Mag. November 1921, p. 800.

origin, for which cubes of the coordinates are negligible, might be represented in five dimensions; but this is not generally true, and unfortunately the simplification is not admissible in the cases of greatest practical importance, *e. g.* the gravitational field of the sun. The theorem itself is correct; but it requires a more general proof.

Take a point on the four-dimensional surface as origin. Let (x_1, x_2, x_3, x_4) be rectangular coordinates in the tangent plane at the origin. The normal is a six-dimensional continuum in which we take rectangular axes $z_1, z_2 \ldots z_6$. Six equations will be necessary to define the four-dimensional surface, and at a regular point these may be taken to be

$$2z_r = a_{r\mu\nu} x_\mu x_\nu + \text{higher powers} \qquad (r = 1, 2 \ldots 6).$$

There are no linear terms in x_μ since deviations perpendicular to the tangent plane are of the second order compared with displacements parallel to the tangent plane. According to the usual summation convention (applying only to Greek suffixes) $a_{r\mu\nu} x_\mu x_\nu$ is summed for values of μ and ν from 1 to 4, and represents a general quadratic function of the x's. By differentiation

$$dz_r = a_{r\mu\nu} x_\mu dx_\nu; \quad dz_r^2 = a_{r\mu\nu} x_\mu dx_\nu \,.\, a_{r\sigma\tau} x_\sigma dx_\tau.$$

Since the geometry of the ten-dimensional space is Euclidean,

$$\begin{aligned} -ds^2 &= dx_1^2 + dx_2^2 + dx_3^2 + dx_4^2 + dz_1^2 + \ldots + dz_6^2 \\ &= dx_1^2 + dx_2^2 + dx_3^2 + dx_4^2 + \sum_r (a_{r\mu\nu} a_{r\sigma\tau} x_\mu x_\sigma) dx_\nu dx_\tau + \text{terms} \end{aligned}$$

containing cubes of the coordinates.

Equating this to $-g_{\mu\nu} dx_\mu dx_\nu$, we have at the origin

$$g_{11} = g_{22} = g_{33} = g_{44} = -1, \quad g_{12} = 0, \text{ etc.}$$

All first derivatives of the $g_{\mu\nu}$ vanish.

The second derivatives are given by

$$\frac{\partial^2 g_{\nu\tau}}{\partial x_\mu \partial x_\sigma} = -\sum_r (a_{r\mu\nu} a_{r\sigma\tau} + a_{r\mu\tau} a_{r\sigma\nu}).$$

When the first derivatives vanish, the Riemann-Christoffel tensor simplifies to

$$\begin{aligned} B_{\mu\nu\sigma\rho} &= \frac{1}{2}\left(\frac{\partial^2 g_{\sigma\rho}}{\partial x_\mu \partial x_\nu} + \frac{\partial^2 g_{\mu\nu}}{\partial x_\sigma \partial x_\rho} - \frac{\partial^2 g_{\mu\sigma}}{\partial x_\nu \partial x_\rho} - \frac{\partial^2 g_{\nu\rho}}{\partial x_\mu \partial x_\sigma} \right) \\ &= \sum_r (a_{r\mu\nu} a_{r\sigma\rho} - a_{r\mu\sigma} a_{r\nu\rho}). \end{aligned}$$

It will be seen that the six z_r's contribute terms to $B_{\mu\nu\sigma\rho}$ which are simply additive. Our subsequent formulæ will involve $B_{\mu\nu\sigma\rho}$ linearly ; so we need consider only one z at a time, and shall accordingly shorten the notation by dropping the r. Thus

$$B_{\mu\nu\sigma\rho} = a_{\mu\nu}a_{\sigma\rho} - a_{\mu\sigma}a_{\nu\rho}.$$

Hence

$$G_{\mu\nu} = g^{\sigma\rho}B_{\mu\nu\sigma\rho} = -a_{\mu\nu}(a_{11} + a_{22} + a_{33} + a_{44}) + a_{\mu\sigma}a_{\nu\sigma}$$

by substituting the Euclidean values of the g's at the origin given above.

In particular

$$\begin{aligned} G_{11} &= -a_{11}(a_{11} + a_{22} + a_{33} + a_{44}) + a_{11}^2 + a_{12}^2 + a_{13}^2 + a_{14}^2 \\ &= (a_{12}^2 - a_{11}a_{22}) + (a_{13}^2 - a_{11}a_{33}) + (a_{14}^2 - a_{11}a_{44}). \quad . \quad . \end{aligned} \tag{1}$$

Also

$$\begin{aligned} G = g^{\mu\nu}G_{\mu\nu} &= (a_{11} + a_{22} + a_{33} + a_{44})^2 - (a_{11}^2 + a_{22}^2 + \ldots + 2a_{12}^2 + \ldots \\ &= -2\{(a_{12}^2 - a_{11}a_{22}) + \ldots (\text{six terms})\}. \quad . \quad . \end{aligned} \tag{2}$$

Hence, since $g_{11} = -1$,

$$\begin{aligned} G_{11} - \tfrac{1}{2}g_{11}G = -\{(a_{23}^2 - a_{22}a_{33}) &+ (a_{24}^2 - a_{22}a_{44}) \\ &+ (a_{34}^2 - a_{33}a_{44})\}. \quad . \quad . \quad . \end{aligned} \tag{3}$$

Consider the *three*-dimensional continuum, which is the section of the world by the plane $x_1 = 0$. This is described by three coordinates x_2, x_3, x_4 and its Gaussian curvature, which we shall denote by $G_{(1)}$, is formed by dropping the terms in G which contain the suffix 1. We see by (2) and (3) that

$$\tfrac{1}{2}G_{(1)} = G_{11} - \tfrac{1}{2}g_{11}G. \quad . \quad . \quad . \quad . \quad . \quad . \tag{4}$$

Since the z_r's contribute linearly to each term in this equation, it holds for six z's as well as for one z.

The radius of (spherical) curvature of a manifold is defined as the radius of a sphere which has the same Gaussian curvature as the manifold. It is easily shown that for the Gaussian curvature $G_{(1)}$ of a three-dimensional manifold, the corresponding radius ρ_1 is given by

$$G_{(1)} = \frac{6}{\rho_1^2}.$$

Thus the result (4) may be written

$$G_{11} - \tfrac{1}{2}g_{11}G = \frac{3}{\rho_1^2}. \quad . \quad . \quad . \quad . \quad . \quad . \tag{5}$$

Consider the quadric

$$(G_{\mu\nu} - \tfrac{1}{2}g_{\mu\nu}G)dx_\mu dx_\nu = 3. \quad . \quad . \quad . \quad . \quad . \tag{6}$$

Setting $dx_\mu=(\rho_1, 0, 0, 0)$ we see by (5) that the equation is satisfied; that is to say, ρ_1 is the radius of the quadric in the x_1 direction. The quadric is seen by inspection of its equation to be invariant; consequently we may take x_1 in any direction we please. Hence the radius of the quadric (6) in any direction is equal to the radius of (spherical) curvature of the corresponding section of the world.

If $G_{\mu\nu}=\lambda g_{\mu\nu}$, then $G=4\lambda$, and the quadric reduces to

$$-\lambda g_{\mu\nu}dx_\mu dx_\nu=3$$

or

$$-ds^2=3/\lambda,$$

showing that the quadric is a sphere of radius $\sqrt{(3/\lambda)}$. Conversely, if the radii of spherical curvature of sections of the world at all points and in all directions are equal to $\sqrt{(3/\lambda)}$, Einstein's equations $G_{\mu\nu}=\lambda g_{\mu\nu}$ will be satisfied. This demonstrates the theorem.

It may be noticed that in this general proof we have substituted spherical curvature for the normal curvature considered in the Appendix to the previous paper. This is necessary because in the general case normal curvature becomes meaningless.

XVI. *On a Type of Oscillation-Hysteresis in a Simple Triode Generator.* *By* E. V. APPLETON, *M.A., M.Sc., Fellow of St. John's College, Cambridge, and* BALTH. VAN DER POL junr., *D.Sc., Conservator Physical Laboratory of Teyler's Institute, Haarlem (Holland)* [*].

THE conditions for the production of free infinitesimal oscillations in various triode circuits have been worked out in great detail during the last few years, but the question of the stability and maintenance of oscillations of finite amplitude does not appear to have received equal attention. In a recent paper [†] we have dealt with the calculation of the amplitude finally attained in a simple case of free triode vibrations in which use was made of a non-linear "oscillation characteristic" easily determined by experiment for any particular tube and circuit. This oscillation characteristic, which represents the relation between the variations of anode potential and of anode current, may be regarded as expressing the electrical properties of an imaginary non-reactive resistance connected in parallel with the inductance of the

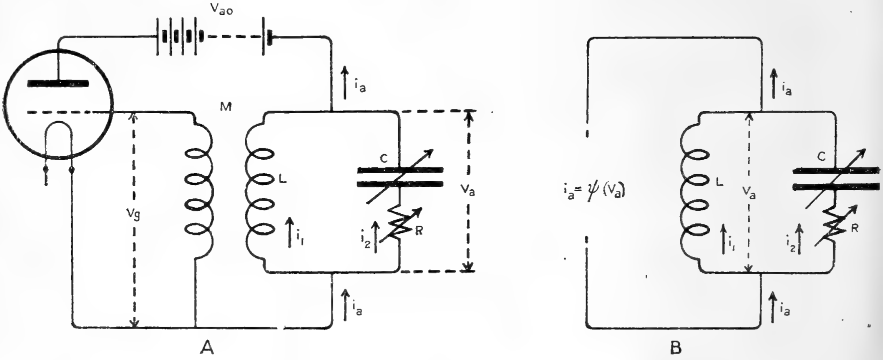
[*] Communicated by Professor Dr. H. A. Lorentz, For.Mem.R.S.

[†] Phil. Mag. vol. xlii. p. 201, August 1921.

oscillatory circuit. The form of the oscillation characteristic may be varied within fairly large limits by adjusting the applied electrode potentials of the triode and the reaction coupling, and thus many interesting problems arise. For example, we may ask ourselves: What must be the shape of the oscillation characteristic such that for some particular set of circuit conditions there may be more than one possible stable amplitude? In such a case we should expect the particular amplitude obtaining to depend on the method of approach to the set of conditions in question. We shall deal here only with the answer to the question for a case in which two stable amplitudes are possible for any given set of circuit constants, but it would not be difficult to extend the analysis to more complicated cases. For example, we find that for two stable amplitudes to be possible, one of which is zero, the expression for the oscillation characteristic, when developed as a Maclaurin series, must have a positive fifth differential coefficient and a negative third differential coefficient. In the case of ordinary receiving triodes we have found it quite easy to obtain characteristics of this particular type, and thus have been able to compare the theoretical results with experiment.

The circuit used throughout the experiments was of the simple type shown in fig. 1 A.

Fig. 1.



A

B

As is well known, the anode current of a triode is a function of both the anode and grid potentials with respect to the filament. But in the circuit of fig. 1 there is a definite relation between the variable parts (v_a and v_g) of the anode and grid potentials, namely

$$v_g = -\frac{M}{L} v_a, \quad \ldots \ldots \quad (1)$$

where grid currents are assumed to be negligible. Thus in such a case the variable part (i_a) of the anode current may be expressed as a function of v_a only, and it is precisely this relation which is represented by the oscillation characteristic mentioned above. In this way we are able to leave out of account the retroactive action of the control electrode, and deal simply with the problem of a conductor possessing a characteristic relation $i_a = \psi(v_a)$ connected to an oscillatory circuit, as shown in fig. 1 B.

It will be seen that the problem we have to discuss is exactly the same as that arising in the case of the dynatron generator of A. W. Hull *, so that the general theory given below will apply *in toto* to both triode and dynatron, if the analogy between the oscillation characteristic of the former and the direct characteristic of the latter is borne in mind. We shall be concerned in general with the determination of the possible stationary amplitudes, and also with the stability of those amplitudes when the characteristic of either generator is given.

The application of Kirchhoff's laws to such a circuit as is shown in fig. 1 B leads to

$$L\frac{di_1}{dt} = Ri_2 + \frac{1}{C}\int i_2 dt = -v_a,$$

$$i_1 + i_2 = i_a = \psi(v_a),$$

which together give

$$\frac{d^2}{dt^2}(v_a + Ri_a) + \frac{d}{dt}\left\{\frac{R}{L}v_a + \frac{\psi(v_a)}{C}\right\} + \frac{v_a}{CL} = 0. \quad . \quad (2)$$

But in the practical case of a high-frequency circuit, Ri_a is small compared with v_a, and thus (2) may be written

$$\frac{d^2 v}{dt^2} + \frac{d}{dt}\chi(v) + w_0^2 v = 0; \quad \ldots \ldots \quad (3)$$

where the subscripts of i_a and v_a have been omitted, w_0^2 has been written for $\frac{1}{CL}$, and $\chi(v)$ has been written for

$$\left(\frac{Rv}{L} + \frac{\psi(v)}{C}\right).$$

We have been unable to obtain a direct solution of (3), but

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* Hull, Proc. Inst. Radio Eng. 6, i. Feb. 1918.

an approximate solution for conditions which closely resemble those of a practical case is possible. Thus in the case of a triode we may consider v as approximately sinusoidal, and equal to $a \sin wt$ since $\chi(v)$ may be regarded as small compared with $w_0 v$. In this way the higher harmonics may be neglected, and an approximate value for the fundamental amplitude in the Fourier expansion for v obtained, where a is regarded as a function of the time t, but such that $\frac{da}{dt} \leqslant wa$, and that $\frac{d^2a}{dt^2}$ is negligible. In accordance with our assumption made above regarding harmonics, we shall retain only the terms involving the angular frequency w.

We thus have

$$v = a \sin wt,$$

$$\frac{dv}{dt} = \frac{da}{dt} \sin wt + aw \cos wt,$$

$$\frac{d^2v}{dt^2} = 2\frac{da}{dt} w \cos wt - aw^2 \sin wt,$$

$$\chi(v) = \sin wt \,.\, \frac{2}{T}\int_0^T \chi(a \sin wt) \,.\, \sin wt \,.\, dt$$
$$+ \cos wt \,.\, \frac{2}{T}\int_0^T \chi(a \sin wt) \cos wt \,.\, dt,$$

and

$$\frac{d}{dt}\chi(v) = w \cos wt \,.\, \frac{2}{T}\int_0^T \chi(a \sin wt) \,.\, \sin wt \,.\, dt$$
$$- w \sin wt \,.\, \frac{2}{T}\int_0^T \chi(a \sin wt) \cos wt \,.\, dt,$$

where T is equal to $\frac{2\pi}{w}$, and $\frac{da}{dt}$ has been neglected in comparison with wa.

On substituting in (3) for v, $\frac{d^2v}{dt^2}$ and $\frac{d}{dt}\chi(v)$, we have

$$aw_0^2 \sin wt - aw^2 \sin wt + 2\frac{da}{dt} w \cos wt$$
$$+ \frac{2w \cos wt}{T}\int_0^T \chi(a \sin wt) \sin wt \,.\, dt$$
$$- \frac{2w \sin wt}{T}\int_0^T \chi(a \sin wt) \cos wt \,.\, dt = 0. \quad (3\text{A})$$

We may here note that the last term in the left-hand side of (3A) is small compared with the first two. Thus, on equating the coefficients of terms involving cos wt and sin wt separately to zero, we have

$$w^2 = w_0^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\frac{da}{dt} + \frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \chi(a \sin wt) \sin wt \, . \, dt = 0. \quad . \quad . \quad (5)$$

From (4) we see that to the particular degree of approximation we are considering, the frequency of the free vibrations depends only on the inductance and capacity of the oscillatory circuit, while from (5) we see at once that the stationary values (e. g., a_s) of a are given by the real roots of

$$\frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \chi(a_s \sin wt) \sin wt \, . \, dt = 0. \quad . \quad . \quad . \quad (6)$$

In considering the stability of the oscillations we may imagine the amplitude to be altered slightly from its stationary value by some external means, and investigate whether the amplitude will eventually return to or depart further from its original value. Thus, if we consider a change of amplitude from a_s to $a_s + \delta a_s$, we have from (5)

$$\frac{d\delta a_s}{dt} + \frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \chi\{(a_s + \delta a_s) \sin wt\} \sin wt \, . \, dt$$

$$- \frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \chi(a_s \sin wt) \sin wt \, . \, dt = 0,$$

or

$$\frac{d\delta a_s}{dt} + \frac{\delta a_s}{\mathrm{T}}\int_0^{\mathrm{T}} \chi'(a_s \sin wt) \sin^2 wt \, . \, dt = 0.$$

Now for any amplitude a_s to be stable, $\dfrac{\frac{d\delta a_s}{dt}}{\delta a_s}$ must be negative ; that is to say, we must have

$$\frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \chi'(a_s \sin wt) \sin^2 wt \, . \, dt > 0. \quad . \quad . \quad . \quad (7)$$

Now by partial differentiation, (6) can further be written

$$\frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \chi'(a_s \sin wt) \, . \cos^2 wt \, . \, dt = 0, \quad . \quad . \quad (6\,\mathrm{A})$$

with the aid of which we are able to write (7) more simply as

$$\frac{1}{\mathrm{T}}\int_0^{\mathrm{T}} \chi'(a_s \sin wt) dt > 0. \quad . \quad . \quad . \quad . \quad (8)$$

In the case of a triode, the oscillation characteristic

$i=\psi(v)$ cannot in general be represented by a simple expression, but use may be made of a power series*.

If this series be written as

$$\psi(v)=\alpha v+\beta v^2+\gamma v^3+\delta v^4+\epsilon v^5\ldots,$$

then $$\mathrm{C}\chi(v)=\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)v+\beta v^2+\gamma v^3+\delta v^4+\epsilon v^5\ldots.$$

On substituting for $\chi(v)$ in (6) and (8), we find that the possible amplitudes are given by the real roots of

$$\frac{1}{2}\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)a+\frac{3}{8}\gamma a^3+\frac{5}{16}\epsilon a^5\ldots\ldots\ldots$$
$$+\frac{1.3.5\ldots\ldots 2n-1}{2.4.6\ldots\ldots 2n}\alpha_{2n-1}a^{2n-1}=0, \quad (9)$$

while any amplitude a is stable for which

$$\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)+\frac{3}{2}\gamma a^2+\frac{15}{8}\epsilon a^4\ldots\ldots\ldots$$
$$+\frac{3.5.7\ldots\ldots 2n-1}{2.4.6\ldots\ldots 2n-2}\alpha_{2n-1}a^{2n-2}>0. \quad (10)$$

If the oscillation characteristic is of such a simple form that the power series can be limited to the first three terms, it may be shown that only one stable amplitude is possible for any given set of triode and circuit parameters. Thus in this case (9) reduces to

$$\frac{1}{2}\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)a+\frac{3}{8}\gamma a^3=0,$$

the solutions of which are given by

$$a_1=0,$$

$$a_2{}^2=-\frac{\frac{4}{3}\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)}{\gamma}.$$

But from (10) we see that for an amplitude a to be stable we must have

$$\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)+\frac{3}{2}\gamma a^2>0.$$

Thus in this simple case only one stable finite amplitude a_2 is possible, the conditions being such that $\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)<0$.

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* *Cf.* van der Pol, Radio Review, vol. i. p. 701, Nov. 1920; and *Tijdschrift van het Nederlandsch Radiogenootschap*, Deel i. Oct. 1920.

This is in agreement with the result of the paper (Radio Review, Nov. 1920) mentioned above.

In such a case the limiting conditions for starting oscillations $\left(i.\ e.,\ \frac{\mathrm{CR}}{\mathrm{L}}+\alpha=0\right)$ are exactly the same as the limiting conditions for stopping an oscillation. That is to say, the stationary amplitude is a single valued function of the circuit parameters, and thus, if R or C is varied, the whole process is reversible.

Our experiments have shown, however, that it is often necessary to take at least two more terms in the series to represent the type of oscillation characteristic met with in a practical case, and we shall now consider the amplitude and stability of the oscillations for such a type of characteristic.

From equations (5) and (9) we have at once

$$2\frac{da}{dt}+\left(\frac{\alpha}{\mathrm{C}}+\frac{\mathrm{R}}{\mathrm{L}}\right)a^2+\frac{3}{4}\frac{\gamma}{\mathrm{C}}\,a+\frac{5}{8}\frac{\epsilon}{\mathrm{C}}a^5=0$$

or

$$\mathrm{C}\frac{d}{dt}a^2+\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)a+\frac{3}{4}\gamma a^4+\frac{5}{8}\epsilon a^6=0, \quad . \quad (11)$$

while for any amplitude a to be stable, we must have

$$\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)+\frac{3}{2}\gamma a^2+\frac{15}{8}\epsilon a^4>0. \quad . \quad . \quad . \quad (12)$$

A solution of (11) can be immediately obtained, but for the present discussion such a solution is unnecessary. For example, the stationary amplitudes are given by the real roots of

$$\left(a+\frac{\mathrm{CR}}{\mathrm{L}}\right)a^2+\frac{3}{4}\gamma a^4+\frac{5}{8}\epsilon a^6=0.$$

These may be written

$$a_1{}^2=0,$$
$$a_2{}^2=-\mathrm{A}+\sqrt{\mathrm{A}^2-\mathrm{B}},$$
$$a_3{}^2=-\mathrm{A}-\sqrt{\mathrm{A}^2-\mathrm{B}},$$

where $\mathrm{A}=\frac{3}{5}\frac{\gamma}{\epsilon}$ and $\mathrm{B}=\frac{8}{5\epsilon}\left(\alpha+\frac{\mathrm{CR}}{\mathrm{L}}\right)$,

and the square roots are taken as having a positive real part.

The conditions of stability are given respectively for

$$a_1 \ldots\ldots \frac{5}{8}\epsilon\mathrm{B}=\frac{\mathrm{CR}}{\mathrm{L}}+\alpha>0,$$
$$a_2 \ldots\ldots \epsilon a_2{}^2>0,$$
$$a_3 \ldots\ldots -\epsilon a_3{}^2>0.$$

If we now consider all possible combinations of signs of α, γ, and ϵ, the possibility and stability of the three amplitudes can be tabulated as follows, where it is assumed that $A^2 > B$. When this is not the case, stationary amplitudes a_2 and a_3 are obviously impossible.

	Sign of ϵ.	Sign of γ.	Sign of $\alpha+\frac{CR}{L}$.	Sign of a_2^2.	Sign of a_3^2.	a_1^2.	a_2^2.	a_3^2.
1......	+	+	+	−	−	**stable**	unstable	stable
2......	+	+	−	+	−	unstable	**stable**	stable
3......	+	−	+	+	+	**stable**	**stable**	unstable
4......	+	−	−	+	−	unstable	**stable**	stable
5......	−	+	+	+	−	**stable**	unstable	unstable
6......	−	+	−	+	+	unstable	unstable	**stable**
7......	−	−	+	+	−	**stable**	unstable	unstable
8......	−	−	−	−	−	unstable	stable	unstable

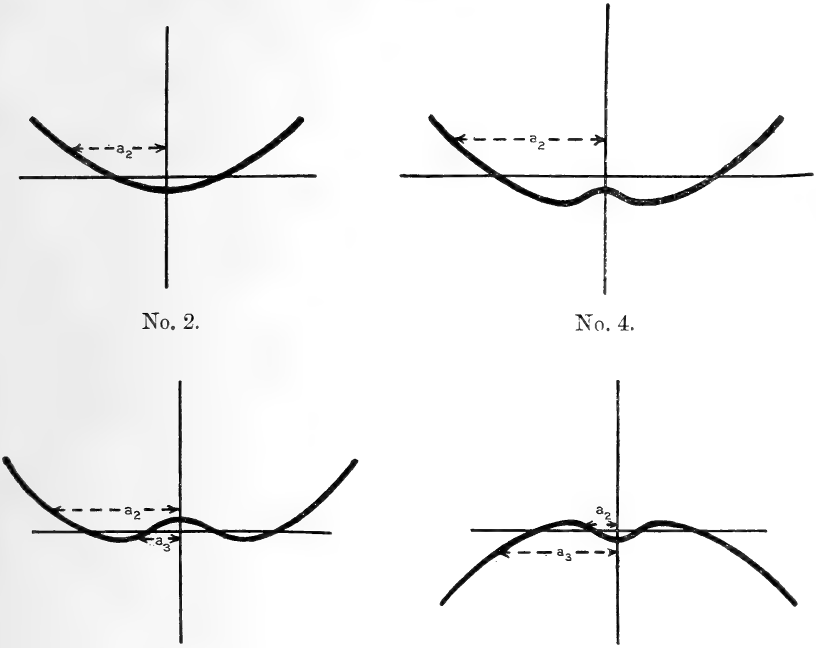
(In this table, amplitudes which are both possible and stable are emphasized by thick rectangles.)

We thus see that the only combination giving *two* possible and stable amplitudes is (3), in which case ϵ is positive, γ negative, and $\left(\frac{CR}{L}+\alpha\right)$ positive. For such a combination of oscillation characteristic and circuit constants the system is stable when not oscillating ($a_1=0$), and also when oscillating with an amplitude a_2. In this case the circuit possesses a positive initial damping coefficient, so that oscillations will not build up automatically, although a stationary amplitude of value a_2, when once produced, will be maintained.

These analytical considerations can further be elucidated in the following way. In (3) $\frac{d\chi(v)}{dt}$ can be written as $\frac{d\chi(v)}{dv}\cdot\frac{dv}{dt}$, where $\frac{d\chi(v)}{dv}$ may be regarded as representing a kind of damping factor which may be either positive or negative, and which, unlike the damping factor used in the ordinary linear treatment of oscillations, is a function of the amplitude. The relation between $\frac{d\chi(v)}{dv}$ and v for cases 2

3, 4, and 6 of the table have been drawn in fig. 2, where the possible amplitudes have also been indicated.

Fig. 2.



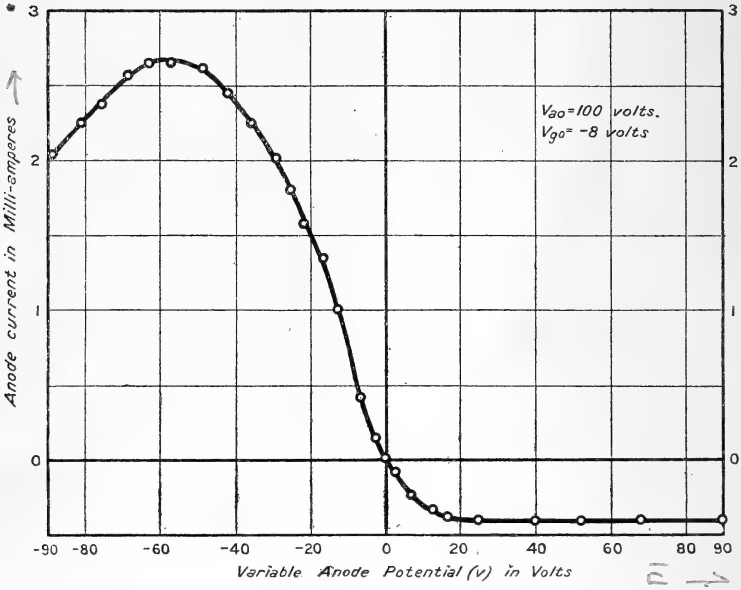
No. 2. No. 4.

No. 3. No. 6.

For any amplitude to be stationary, it follows from energy considerations that the damping term for a cycle of v must be partially positive and partially negative. In this way we see that the amplitudes a_2 and a_3 are possible. In order that the amplitude should be stable, however, it is necessary that, if the amplitude of v increases, the damping factor $\frac{d\chi(v)}{dv}$ should be positive over a greater part of the cycle of v and *vice versâ*. Thus a_2 is stable in Nos. 2, 3, and 4 but not in No. 6. In the same way a_3 is stable in No. 6 but not in No. 3.

In fig. 2 the function $\frac{d\chi(v)}{dv}$ has been made symmetrical with respect to the axis $v=0$, since from (9) and (10) it is seen that, so far as our present approximations go, the even terms (*e.g.*, β, δ, etc.) of the series for the oscillation characteristic can be neglected. We may obtain a derived oscillation characteristic in which these terms are excluded by means of a simple graphical method. A typical oscillation characteristic obtained experimentally is shown in fig. 3, for which the value of $\frac{M}{L}$ is 0·57 and the steady electrode potentials such as to give a case of marked oscillation hysteresis.

Fig. 3.



We have eliminated the even part in the function representing this curve by folding the curve about the i axis and then again about the v axis, and taking the mean of the two ordinates occurring in the quadrants II. and IV. The result is shown in fig. 3A. The general agreement between the differential coefficient of this symmetrical curve which represents the relation $i=\psi(v)$, and the curve of No. 3, fig. 2, is clearly apparent if we bear in mind that $\chi'(v)$ is equal to $\frac{R}{L}+\frac{\psi'(v)}{C}$.

We are now prepared to discuss in greater detail the quantitative results previously obtained for our example of Case 3 of the table and No. 3 of fig. 2.

Fig. 4 shows a graphical representation of these results, in which the square of the amplitude is plotted as a function of B. It may here be noted that in a practical case, B may be varied continuously by varying the resistance R or the capacity C of the oscillatory circuit.

Fig. 3 A.

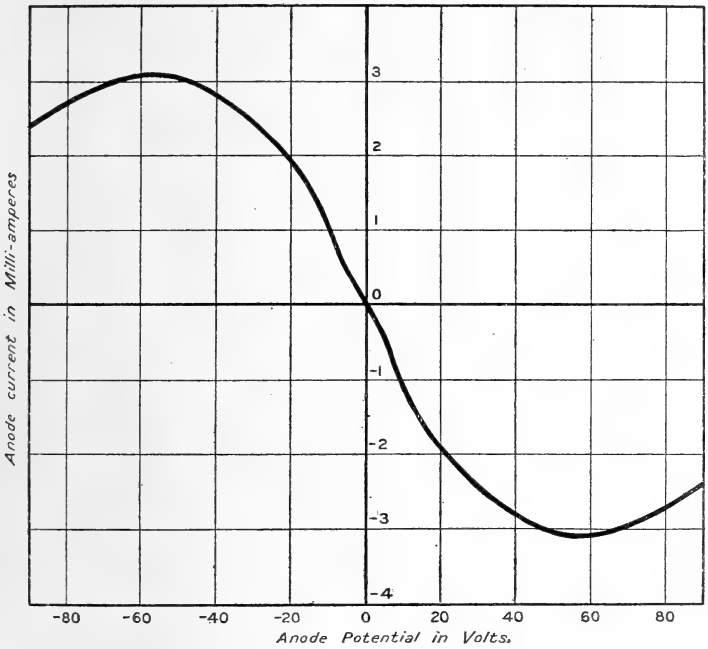
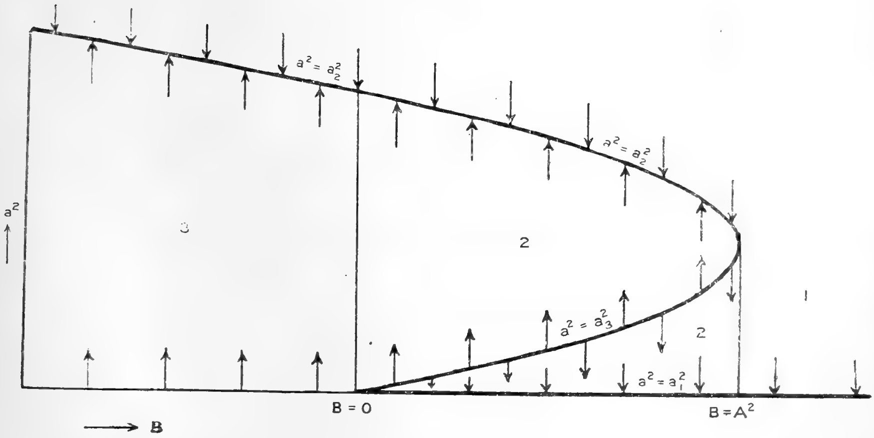
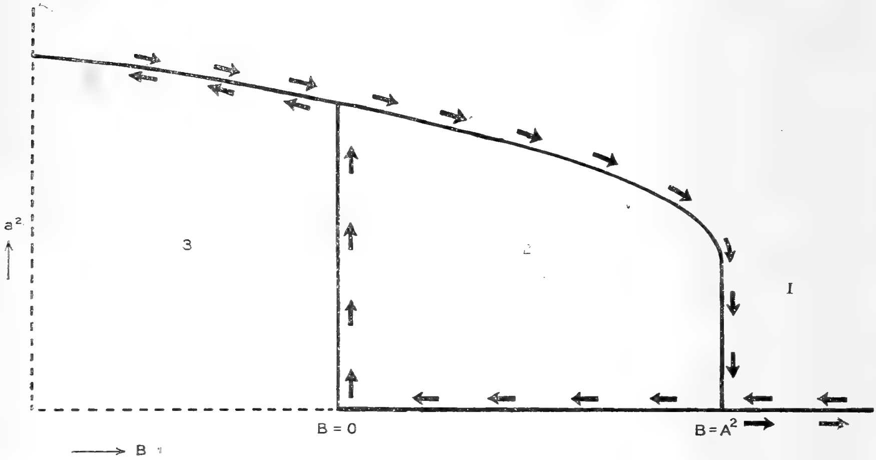


Fig. 4.



For all values of B for which $B > A^2$ (Region 1), we see that the roots are either zero or imaginary, so that no sustained oscillation is possible. In Region 2, however, for which we have $A^2 > B > 0$, various possibilities arise according to the initial value of a^2. If the initial amplitude is small so that $a_2^2 > a_3^2 > a^2$, we see from (11) that $\frac{d}{dt}a^2 < 0$, and thus the amplitude will tend to decrease to zero as indicated by the arrows. If, however, the initial amplitude is such that $a_2^2 > a^2 > a_3^2$, then $\frac{d}{dt}a^2 > 0$ and the amplitude will increase to a_2. Further, if $a^2 > a_2^2 > a_3^2$, then $\frac{d}{dt}a^2 < 0$ and the amplitude again finally reaches a_2. We thus see that in Region 2 no finite stable amplitude will be reached automatically unless by some external agency we succeed in producing in the system an amplitude a such that $a^2 > a_3^2$, in which case the amplitude automatically builds up to the stable value a_2. For any gradual variation of B after such an amplitude has once built up, the amplitude value a_2 is maintained.

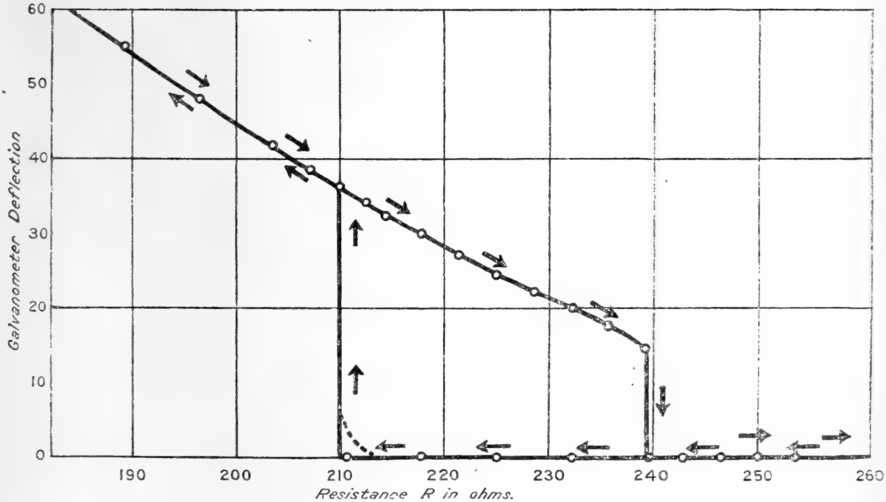
Fig. 5.



As a method of testing this theory, we may imagine a cycle of operations in which B is varied from a large positive value to a negative one, and then the process reversed. We see from the above discussion that the cycle will be irreversible and of the type illustrated in fig. 5, where the relation between a^2 and B is shown. The value of B may be most easily varied in a practical case by means of a variation of C the capacity, or R the resistance of the oscillatory circuit. A cycle of the type indicated in fig. 5 was accordingly carried out for a circuit of the type shown in fig. 1, A, the amplitude of the oscillations being indicated by means of a crystal detector and galvanometer connected in series with a coil which was loosely coupled with the oscillator circuit. Fig. 6 shows the relation obtained between the galvanometer deflexion and the value of R. The general agreement with the theoretical curve of fig. 5 is at once apparent.

For certain types of oscillation characteristic we found evidence of the possibility of two stable amplitudes of the same frequency, both differing from zero for a given set of circuit parameters. For example, it was sometimes found that on decreasing the resistance R a small oscillation started before the resistance value equivalent to B=0 was reached. This effect is illustrated by the dotted line in fig. 6. It was also found that if the resistance was not

Fig. 6.



allowed to become less than that represented by B=0 (fig. 5), the relation between amplitude and resistance was reversible. It is clear that two more terms are necessary in the series for $\psi(v)$ to account for this effect. We have thus evidence of a phenomenon depending on the value of the *seventh* differential coefficient of the oscillation characteristic.

In the theoretical discussion given above, it was found that for conditions represented by Region 2 (see fig. 4) it should be possible to start a stable oscillation by means of an electrical impulse greater than a certain amount. This theoretical prediction was experimentally verified in a qualitative way by using transient induced electromotive forces produced with the aid of a coil and a bar magnet.

From the point of view of certain practical applications of triodes (such as triode relays and quiescent aerial telephony), it is of interest to consider how the difference between the limiting parameters necessary for starting an oscillation and those necessary for stopping one vary with the values of the maintained electrode potentials of the triode. Experiments were therefore carried out to test this point.

A triode that had been previously carefully tested for steadiness was used in the circuit of fig. 1, care being taken to allow the thermal conditions of the triode and its supports to become steady before measurements were made. The resistance R of the oscillatory circuit was non-inductive ($CuSO_4$ solution) and continuously variable. The values of the limiting resistances for starting and stopping an oscillation were found for various values of the applied steady grid potential v_{go}. The existence of a sustained oscillation was indicated both by means of an autoheterodyne circuit some metres away and also by means of a loosely-coupled sensitive detector-galvanometer circuit. The experimental results are indicated in fig. 7, where the ordinary grid potential-anode current characteristic is also shown.

It will be seen that there is a region of grid potentials (*e. g.*, from -5 to $+1$ volts in fig. 7) in which the limiting resistances for starting and stopping the oscillations are the same. For these values of grid potential the relation between the oscillation amplitude and the resistance was quite reversible, no hysteresis of the type illustrated in fig. 5 being apparent.

For other values of grid potential the limiting conditions for starting and stopping an oscillation were not the same. For such cases, evidence of oscillation hysteresis could always be obtained. It was also noticed that in every case the oscillations started suddenly with a large amplitude, when the value of R was continuously reduced to the critical value (R starting) shown in diagram, and that also on increasing R again the amplitude fell suddenly to zero when a certain value (R stopping) was reached.

More careful experiments were afterwards carried out to test whether the limiting conditions for starting and stopping the oscillations for the region between -5 and $+1$ volts (fig. 7) were exactly the same. In these experiments the conditions were altered by varying the oscillatory circuit capacity C. The spindle of the air-condenser used for this purpose was turned by means of a long handle, the end of which could be moved through small distances by means of a micrometer screw. In this way it was shown that the difference in the critical capacities for

Fig. 7.

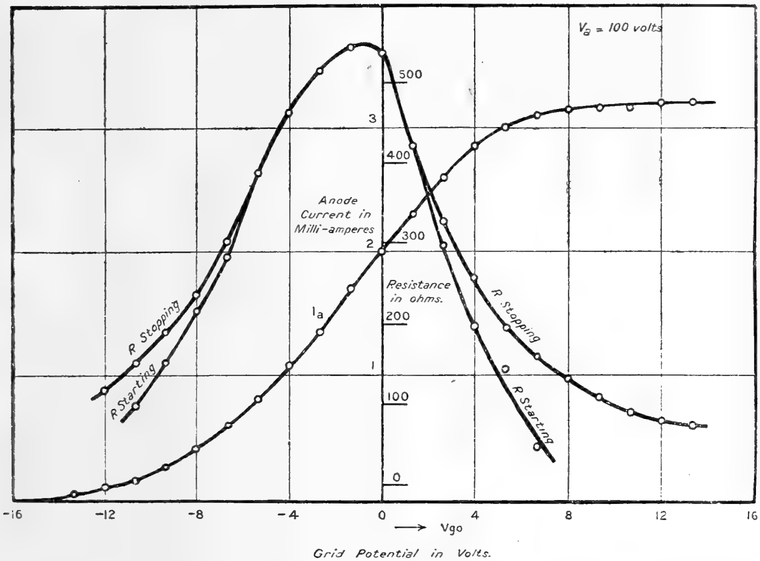
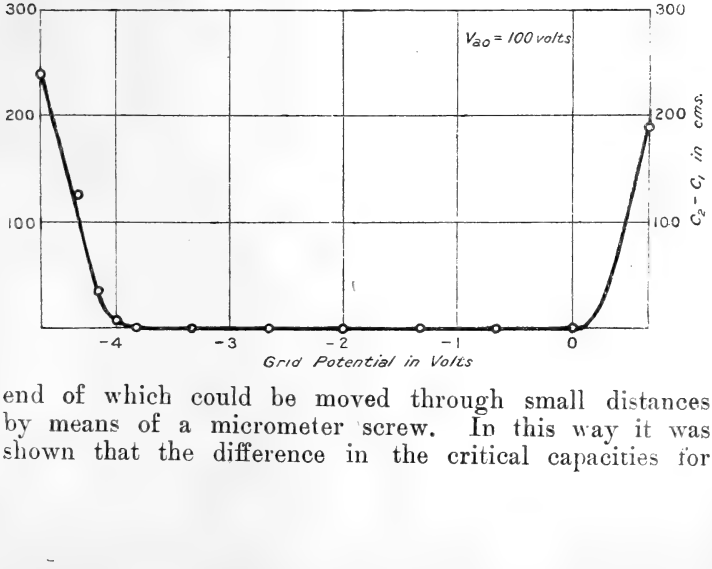


Fig. 8.



starting (C_1) and stopping (C_2) the oscillations, expressed as a fraction of the total capacity, was certainly less than $\frac{1}{10,000}$. It thus seems certain that for this region of grid-potential values we are dealing with cases in which the values of ϵ and γ in the series for $\psi(v)$ are both positive, and that for this region no oscillation hysteresis exists.

The actual observations are shown in fig. 8, in which the ordinates represent the difference (C_2-C_1) in the critical capacities for starting and stopping oscillations and the abscissæ grid potentials.

The agreement of experiment with the theory given above was finally tested in another way. From the solution of (12) we have for any oscillation characteristic with which oscillation hysteresis is marked

$$\frac{CR_1}{L}=-\alpha$$

and

$$A^2=\frac{8}{5\epsilon}\left(\alpha+\frac{CR_2}{L}\right),$$

where R_1 and R_2 are respectively the critical resistances for starting and stopping an oscillation. From these relations we have

$$R_2-R_1=\frac{5\epsilon A^2L}{8C},$$

so that the difference between the critical resistances should be inversely proportional to the capacity of the oscillatory circuit. Experiment showed this to be the case.

Summary.

A general non-linear theory of a simple triode generator is developed, from which the possible and stable amplitudes of the generator may be determined when the form of the oscillation characteristic is given. The conditions necessary for the possibility of two stable amplitudes for the same set of tube and circuit parameters are examined, and it is found that for two stable amplitudes to be possible, one of which is zero, the expression for the oscillation characteristic, when developed as a Maclaurin series, must have a positive *fifth* differential coefficient and a negative *third* differential coefficient. Experiments confirming this theory for such cases are described, in which it is shown that the relation between the oscillation amplitude and one of the circuit parameters (*e. g.*, resistance or capacity of the oscillatory

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circuit) is irreversible, so that for certain values of this parameter the amplitude may be either zero or finite according to the method of approach to the set of conditions in question.

It is shown theoretically that in such cases of irreversibility it should be possible to cause the amplitude to jump from the zero to the finite value by means of an electrical impulse greater than a certain amount. Experimental confirmation of this was obtained by using the transient electromotive force from a coil and moving bar magnet.

The relation between the critical parameters for starting and stopping oscillations and the maintained electrode potentials has been investigated experimentally, and it is found that there is usually a region of grid potential in which the amplitude is a single-valued function of the circuit parameters, so that here the conditions for starting and stopping oscillations are the same. For such values of grid potential it may be concluded that the oscillation characteristic may be approximately represented by a simple power series of *three* terms.

For other values of grid potential a difference in the critical circuit constants is found, always accompanied by the possibility of oscillation-hysteresis. A simple power series of *five* terms for the oscillation characteristic must be used to account for the phenomena in such cases.

Experimental evidence of the possibility of two stable amplitudes, both differing from zero, has also been obtained This is a phenomenon depending on the *seventh* differential coefficient of the oscillation characteristic.

Teyler's Stichting,
Haarlem, Holland.

XVII. *Polarization Phenomena in X-Ray Bulbs.* By S. Ratner, *University of Manchester* [*].

Introductory.

1. HITHERTO the sparking potential in well exhausted vacuum tubes has been considered to be the property of the gas in the tube, being determined entirely by the nature and the pressure of the gas. It has been noticed that gases occluded by the electrodes facilitate the discharge, but only in so far as they increase the pressure

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[*] Communicated by the Author.

on being released from the electrodes during discharge. The nature of the electrodes themselves, according to all experimental data, has but little influence upon the sparking potential and upon the amount of the current which flows through the tube.

In the course, however, of some experiments with an X-ray bulb through which a continuous discharge was maintained for a long time, the writer has observed a gradual hardening of the bulb in spite of the maintenance of a comparatively high pressure which could be controlled throughout the experiments by a Gaede pump and measured by a McLeod gauge connected to the bulb. Further experiments carried out in this direction have revealed a remarkable effect which takes place in an X-ray bulb or, more generally, in any vacuum tube after a sufficiently long and constant run. This is, that after a discharge has been kept running long enough, a time arrives where the resistance of the bulb begins to increase gradually, and finally becomes sufficiently high to stop the discharge altogether, although the pressure still remains constant and comparatively high. This phenomenon is somewhat analogous to the polarization of an electrolytic cell, and for the sake of brevity shall, in what follows, be referred to as a polarization effect.

The present paper contains a description of the procedure by which an X-ray bulb may be polarized, as well as the results of some experiments carried out with such a bulb.

Apparatus and Procedure.

2. The bulb used was constructed for other purposes, being of the type described by Rausch von Traubenberg *.

The aluminium cathode C (fig. 1) is introduced into the bulb by means of the ground joint G. The anode consists of a slightly inclined copper plate A, 5 cm. in diam., fitting into the bottom of a brass cylinder B, 4 cm. long, into which the neck of the bulb is sealed with white wax. This cylinder has a narrow slit S, about 4 cm. long, cut round the cylinder and covered with thin aluminium foil, through which the beam of X-rays could pass with very little absorption. Plates of aluminium of different thicknesses could be put between the aluminium window and a fluorescent screen placed in a dark camera (not shown in the figure)—an arrangement by means of which the penetrating power of the X-ray beam could be roughly estimated. The

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* Rausch von Traubenberg, *Phys. Zeits.* xviii. p. 241 (1912).

anode A and the cylinder B are surrounded by water-cooling jackets W. The bulb is connected to a discharge-tube R, 14 cm. long and 5 cm. diam., with two large aluminium electrodes sealed into the tube and provided with water jackets. These electrodes are identical in size and shape, so that the current in the tube may be reversed without changing in any way the conditions of the discharge. The whole is connected to a Gaede mercury pump and McLeod gauge.

The apparatus always contains some vapour from sealing-wax and tap grease, which, if not constantly pumped out, slowly accumulates, reaching in one or two days a maximum value of about ·015 mm.; but it could be made so airtight that this maximum pressure was never exceeded, even when the bulb was not pumped out for several weeks. The accumulation of the vapour is fortunately a slow process, as is shown by the fact that with the pump constantly working, a pressure could be easily reached which is too small to detect by the McLeod gauge. The presence, however, of mercury vapour in the apparatus was unavoidable.

Under the discharge large quantities of gases are constantly being evolved from the glass and metal parts. The evolution of these gases, although diminishing with usage, always remains appreciable, necessitating the constant use of the pump during the discharge. By varying the speed of the pump and controlling the stop-cocks, the pressure in the bulb could, however, be regulated and kept sufficiently constant. Before taking pressure readings the discharge was interrupted, and the pump stopped in order to avoid the effect of spark-pressure * and to ensure an even distribution of the gas throughout the apparatus.

After the discharge through the bulb had been maintained for a sufficiently long time, the pump constantly working at full speed, the pressure, which at first is considerable, begins to diminish, finally reaching a value of some thousandths of a millimetre, and at this stage of exhaustion a beam of X-rays of increasing penetrating power begins to pass through the aluminium window. At the same time, the sparking potential across the bulb gradually increases, and in order to maintain the discharge, it becomes necessary to regulate the gas-pressure, keeping it constant above a certain lower limit.

If, now, the discharge is further maintained for a long time, the following effect is observed: the sparking potential begins to increase markedly, the current through the bulb

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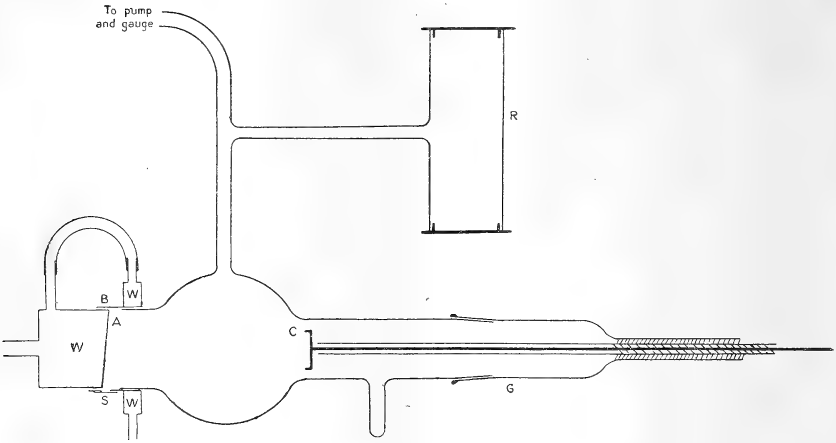
* J. J. Thomson, 'Electricity through Gases,' 2nd ed. p. 516.

diminishes, and the beam of X-rays from the aluminium window becomes more penetrating *in spite of the maintenance of a constant pressure in the bulb.* The potential difference across the bulb must then be gradually increased, and finally a time arrives where the highest voltage supplied by the coil is insufficient to break down the bulb's resistance, and the discharge ceases. In order to maintain the discharge, it is now necessary to increase the pressure, but after a further long run the resistance of the bulb becomes again too high, and the pressure must be raised still further. By repeating this operation several times, a stage is ultimately reached where a p.d. of more than 50,000 volts was not sufficient to produce a discharge, the pressure in the bulb being as high as ·065 mm.

Fig. 1.



When the bulb is approaching this stage of polarization, the discharge usually shows an increasing tendency to choose an alternative path through the bulb, starting not from the cathode itself, but from a point on the rod supporting the cathode. This lowers the sparking potential and introduces some other complications in the progress of the experiments. This tendency is especially well marked when the exhaust-tube leading to the pump ends in the neck of the bulb opposite the rod. If the rod be enclosed in a glass tube, this tube usually cracks and the discharge passes through it. It was found, however, in the course of the experiments that this troublesome effect could be completely eliminated by covering the rod with a stout glass tube and evacuating the bulb through a side tube fused into the middle of the bulb, as shown in the figure.

The following data, taken from one set of experiments, give some idea of the time the discharge must be passed through the bulb before the various stages of polarization are reached. The experiments began with a new bulb, and after a run of about eight hours daily during three consecutive days, the exhaustion of the bulb became high enough to produce X-rays. Two days later a penetrating beam of X-rays could be observed to pass through the aluminium window, the pressure in the bulb being ·003 mm. and the p.d. about 15,000 v. After a further run for three days the polarization effect became well marked, and the pressure had then to be raised to ·012 mm. and the p.d. increased. On the following day a degree of polarization was reached where a p.d. of more than 50,000 v. could not break down the resistance of the bulb at a pressure as high as ·035 mm., and a few hours later the minimum pressure at which the same p.d. could produce a discharge was of the order of ·060 mm.

The current supplied by the induction-coil used in these experiments was comparatively small, not exceeding 3×10^{-4} amp. when the bulb was well exhausted. It was noticed, however, that with larger currents the same effect is reached in less time; and it seems very probable that different stages of polarization are reached only after definite quantities of electricity have passed through the bulb.

If the current be reversed, it passes freely through a polarized bulb. Experiments with the discharge-tube R, where the anode and the cathode are identical in size and shape, show that a vacuum tube may be polarized only in one direction. When the current is reversed, even for a short time, the polarization of the bulb becomes greatly reduced, and a run in the former direction is then necessary to bring the bulb back to the same stage of polarization. Attempts to carry the experiments further in order to reach a higher degree of polarization were hampered by the fact that with increasing pressure in the bulb it becomes more and more difficult to rectify the current by means of an ordinary rectifying valve or a spark-gap used in these experiments. The use of a thermionic valve might remove this difficulty.

When the discharge in a polarized bulb ceases, a small current of the order of 1 per cent. of the normal value may still be detected by a galvanometer. This residual current persists, even at the highest exhaustion of the bulb, and is probably due to conduction by the walls of the bulb.

Recovery of a Polarized Bulb.

3. A polarized bulb when left to itself gradually returns to its normal condition. The rate of recovery may be investigated by studying the resistance of the bulb at definite intervals after a certain stage of polarization has been reached and the discharge interrupted. One set of experiments of this kind gave the following results:—A degree of polarization was first produced where, with a pressure of ·042 mm., the necessary sparking potential was equivalent to a spark length of 14 cm. After an interval of 5 minutes the sparking potential as measured by the spark length fell to 12 cm., and after intervals of 15, 30, 45, and 60 minutes the corresponding sparking potentials were 10, 7, 4·5, and 2·5 cm. Left overnight the bulb was found to be completely depolarized, so that a p.d. of 1500 v. could again produce a normal discharge.

More accurate experiments in this direction were now carried out under conditions where a comparatively small potential difference could produce a discharge, and in this case a battery of small accumulators could be used instead of the induction-coil and the potential difference measured with accuracy. The experiments are based on the fact that if in a polarized bulb the pressure be slightly increased by introducing gas from outside, the sparking potential falls abruptly, whereas the resistance of the bulb still remains considerable and manifests a gradual decrease with time, characteristic of the resistance of a polarized bulb. If, now, at definite intervals of time, different voltages taken from the battery be put across the bulb and the currents produced by the discharge measured, the results may supply definite data for the determination of the rate of recovery of the bulb. Table I. shows the results of one set of these experiments. In column t. the intervals of time in minutes are given; in columns C 3500, C 2500, and C 1500 the current through the bulb in hundredths of a milliampere, the p.d. applied being 3500, 2500, and 1500 v. respectively.

Table I.

t.	C 3500.	C 2500.	C 1500.
1	2	—	—
5	8	3	—
10	22	14	4
20	58	34	16
40	110	78	46
60	160	105	76
120	195	130	95
240	215	160	125

The bulb in the experiment was polarized at ·050 mm., and this pressure raised to ·072 mm. by introducing air from outside. Dashes in the columns C indicate that the corresponding p.d. was not sufficient to produce a discharge. The table shows that the rate of recovery of the bulb, at first large, decreases with time, and that in two hours the bulb practically returns to its normal condition. It must be pointed out, however, that the results of different sets of experiments of this kind are not very consistent with each other.

The rate of recovery of the bulb, in fact, depends largely on the pressure inside; for, if an amount of gas sufficient to raise the pressure to several millimetres be introduced into the bulb from outside, and then rapidly pumped out, the bulb returns at once to its normal condition; while, on the other hand, the same stage of polarization may persist for several hours if the bulb be kept well exhausted.

After a bulb has recovered to its normal condition, it may easily be brought back to a state of polarization by a comparatively short run.

Part played by Gases in the Bulb.

4. It seemed at first natural to suppose that polarization is due entirely to changes in the nature and the properties of the gases brought while the discharge takes place. It might be, for instance, that the gases evolved from the electrodes consist of helium or neon whose sparking potentials at sufficiently low pressure are much higher than that of air, or that the gaseous molecules exhibit some properties of fatigue to the process of ionization, since after a sufficiently long run the same molecules necessarily have to be ionized several times. Various experiments carried out in this direction have shown, however, that the gases themselves play but a small role in the phenomenon. For firstly, as shown above, after the introduction of air from outside the bulb still remains polarized. Moreover, in some experiments a minute quantity of air was allowed to leak through an insufficiently greased tap, and the state of polarization was still reached in spite of the fact that under these conditions there was a continuous flow of fresh gas from outside. The most convincing experiments in this direction were made by connecting the bulb to the side tube R. A state of polarization was reached where the highest voltage supplied by the coil could not produce a discharge through the bulb at a pressure of ·060 mm., and it was then found that a potential difference

of 1200 v. put across the side tube produced a normal discharge through it. Since the pressure and nature of the gas in the side tube was essentially the same as in the main bulb, these experiments furnish a definite proof that the phenomenon of polarization is not brought about by the gases in the bulb. The effect must be traced back to changes in the nature of the electrodes caused by prolonged electronic action.

Later experiments have shown, however, that even small quantities of water-vapour exercise a marked influence in the phenomenon. When a small quantity of this gas is introduced into a polarized bulb, the polarization is at once considerably reduced, and the bulb has then to go through a long run before the previous stage is again reached. It thus seems as if the electrodes were in some way affected by the water-vapour losing the properties acquired during the process of polarization.

An attempt was also made to study the polarization effect with different gases in the bulb. These experiments, however, proved to be impossible when bulbs such as those described in this paper are used, since the gases which are constantly evolved during the discharge render those initially filling the bulb impure.

When observed in the dark, it is seen that the shape and colour of the luminous column in the discharge undergoes considerable changes as polarization sets in, but a spectroscopic study of this effect has not yet been made.

Effect of change of Cathode.

5. In the experiments described so far, only aluminium cathodes were used. Since now, as has been shown, polarization is caused by changes in the nature of the electrodes, it seemed important to repeat some of the experiments, using other metals as cathodes. Before starting these experiments, difficulties were anticipated from the disintegration of the cathode, and consequently in the first place copper was chosen, as being less liable to sputter. The first experiments were unsuccessful. A thick layer of sputtered metal was soon deposited on the walls of the bulb, and after a run of several days a well-marked layer was formed also on the neck of the bulb behind the cathode. Finally the current through the bulb was found to be conducted entirely by the metal film connecting the anode with the cathode, and the experiments had to be abandoned. Later on, however, a

simple arrangement was found by means of which this difficulty could be avoided. A circular piece of mica was fixed on the rod supporting the cathode a few cm. behind it, so as to screen the neck of the bulb from the sputtering particles of the cathode. With this arrangement it was found possible to carry on the experiments until polarization of the bulb was reached. The degree of polarization, however, was far from being as high as previously described, and when the highest voltage was applied the maximum pressure at which the discharge failed to pass was only ·030 instead of ·065 mm. in the former case. Further experiments have shown that this cannot be ascribed to the change in the metal of the cathode. The conditions of the discharge were changed considerably in these experiments, owing to the formation in the bulb of a metal film in contact with the anode, thereby practically transferring the whole bulb into one large anode, which in some parts approached the cathode. When, again, an aluminum cathode was re-introduced into the bulb in place of the copper one, the same lowering of the degree of polarization, more or less, was still observed.

An attempt was also made to repeat the same experiments with a sodium cathode, in view of the peculiar electric properties of the alkali metals. The cathode was cut from a large piece of sodium under benzol, and then quickly introduced into the bulb, so that a fairly fresh surface of sodium was obtained. The experiments with this cathode were, however, difficult and the results somewhat doubtful, owing to the low melting-point of sodium. Only small currents could be passed through the bulb on account of the melting of the cathode and the accumulation of sodium vapour. Finally, a stage was reached where a p.d. of about 20,000 v. was insufficient to produce a discharge at a pressure of ·015 mm.

Experiments with source of Ionization inside the Bulb.

6. Interesting results which have a bearing on the theory of the phenomenon were obtained by introducing a source of ionization into the bulb. A small disk coated with polonium was placed in the middle of the bulb, and the gas exposed to the action of α-particles. At such a low pressure the ionization could not be intense, but still a certain number of ions were constantly being produced in the apparatus. This, however, did not affect the experiment, and after a sufficiently long run a high degree of polarization was still reached at a pressure of about $\frac{1}{15}$ mm. Under these

conditions the electric field betwen the electrodes was more than a hundred times as great as that required by positive ions producing ionization by collision, and the free path of the ions was small compared with the dimensions of the bulb, so that independently of any electronic emission from the cathode a sufficiently large current would be expected to flow across the bulb. In fact, however, when polarization was reached, the current through the bulb was as small as 10^{-8} amp., and, as mentioned above, was carried entirely by the glass, since it did not appreciably diminish when the bulb was thoroughly exhausted afterwards. These results are very striking if we bear in mind that at the same pressure under ordinary conditions a p.d. of less than a thousand volts is sufficient to produce a large current which, according to present theories, is carried entirely by ions produced by collision.

Discussion of Results.

7. The experiments described in § 4 are sufficient evidence that polarization phenomena originate solely with the electrodes. Now, internal changes in the electrodes could hardly be caused by the discharge, and it seems more likely that the phenomenon is due to the destruction by electronic action of the gaseous layers in the surface of the electrodes. These layers, whose existence is now well established, play an important part in various phenomena. It has long been well known that gases occluded in the electrodes greatly facilitate the passage of a discharge through a vacuum tube, and it has been found recently that metal surfaces carefully freed from gases do not exhibit any appreciable photoelectric effect *. It seems therefore, as if the process of electronic emission from cold metal surfaces could take place only through the intermediary of the surface-layer of gaseous molecules.

This theory may serve as a guide in interpreting the phenomena described above. During the discharge the gaseous layer on the surface of the cathode undergoes a continuous disintegration, which, after a long run, begins to affect the electronic emission from the cathode and finally causes the discharge to stop altogether. After the discharge is interrupted, a new layer of molecules on the surface of the cathode is gradually built up, which brings the polarized bulb back to its normal condition. The larger the pressure in the bulb the quicker this new layer

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* Hallwachs, *Phys. Zeits.* Nov. 1920.

would be re-established, and this is in good agreement with the results. The fact that a bulb is polarized in only one direction may be explained by supposing that the action of electronic bombardment on the anode is not sufficient to destroy the gaseous layer on its surface. The effect of water-vapour mentioned in § 4 shows that this gas is capable of forming a layer on metal surfaces with much greater ease than other gases.

It is possible that the presence of gaseous layers on the electrodes also plays an important part in their absorption of the electric charges which are carried by the ions. The well-known phenomenon of double electric layers on metal surfaces shows that an encounter between an ion and a metal surface is not necessarily followed by the transference of the electric charge from the former to the latter. It is possible that when the gaseous layer on the cathode is disintegrated, the positive ions striking against it are unable to impart their charges to it, but rather form a positive electric layer very close to its surface, and that this layer causes the polarization of the bulb. This assumption could be tested experimentally; for, firstly, the cathode fall of potential would be expected from this point of view to remain constant, or even to increase when the state of polarization sets in and a high p.d. put across the bulb fails to produce a discharge through it. The theory may also be checked by introducing into the bulb a heated platinum strip coated with a salt emitting positive ions; for, if then the bulb be polarized and a p.d. established between the cathode and the hot platinum strip as an anode, the positive emission from the strip should not be expected to produce a current through the bulb. Experiments in this direction are now in progress.

Hardness of a Polarized Bulb.

8. As mentioned above, after a sufficiently long run the beam of X-ray emitted by the bulb exhibits a well-marked tendency to increase in penetrating power in spite of the maintenance of comparatively high pressures, and when the bulb is polarized, very penetrating rays may be produced at pressures as high as $\frac{1}{15}$ mm. The experiments show, in general, that the hardness of the rays is determined entirely by the potential difference and is independent of the pressure, which is not a little surprising if we bear in mind that under the conditions of the experiments the electrons had to undergo a considerable number of collisions with the gaseous molecules before reaching the anode. It must be assumed

either that the free path of the electrons is at least a hundred times as large as that of the molecules, or that a larger proportion of the electrons do not lose any appreciable part of their energy upon collision.

In view of the above, a question arises as to the gradual hardening of an X-ray bulb with usage. It is usually assumed that the cause of this is the disappearance of the gas in the bulb, but this assumption is not based on direct experiments. It seems more probable that the gradual hardening is due to the phenomenon described in the present paper.

My thanks are due to Prof. W. L. Bragg for the interest he has taken in this work.

The Physical Laboratory,
Victoria University,
Manchester.
July 1921.

XVIII. *Röntgenograms of Strained Crystals. By* A. F. JOFFE, *Member of the Russian Academy of Sciences, Director of the Röntgenological and Radiological Institute, Petrograd, and* M. V. KIRPITCHEVA *.

[Plate II.]

I. *The Residual Strain.*

IT is a well-known fact that several crystals are capable of undergoing a residual strain without any apparent loss of their integrity. Thus, for instance, rock-salt becomes plastic like wax on being warmed or under the action of a slowly increasing load. In spite of numerous investigations on the nature of these strains by crystallographers, the question how the structure of the crystal can remain deformed after strain, when no external forces exist, remains unanswered. An investigation of the crystal between crossed nicols shows that great internal stresses, which might explain the strain, do not exist in it. The supposition that a sliding of separate layers of the crystal along the plane of the rhomboic dodecahedron takes place in such a manner that the regularity of the crystalline grating remains in spite of the external change of form, is shown not to hold by the fact that on bending a crystal of

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* Communicated by Prof. Sir E. Rutherford, F.R.S.

rock-salt the crystal breaks not along planes, but along curved surfaces, which do not straighten under a prolonged annealing.

To solve this question we have used Laue's röntgenograms, observing the picture on a fluorescing screen or on a photograph. It is most simple to study a homogeneous strain (*e.g.* a compression) of rock-salt, loading it gradually by means of an electromagnet.

After the limit of elasticity is passed, the separate spots of Laue's röntgenograms begin to elongate and to form the figure shown on the accompanying photograph (Pl. II.). The detailed photograph of a crystal not too much strained shows in every elongated spot a stratification, consisting of a series of separate spots the number of which increases with the increase of the strain. Every such beam is at the same time a spectrum (which can clearly be seen on the photograph), but it is easy to observe that the stratification is due to separate small crystals, into which the whole crystal has parted, and is not a line spectrum of Röntgen rays. The dimensions of the fragments are a few hundredths of a millimetre.

On the fluorescing screen and on the photograph the direction in which the small crystals slide can be seen. The spot corresponding to the rhombical dodecahedron (110) remains completely unaltered, while the others become elongated. The direction of the stratification in every beam also shows the direction around which the rotation of the little crystals takes place. Thus we come to the conclusion that a crystal of rock-salt when compressed breaks up into small crystals, which, while sliding along the plane of the rhomboic dodecahedron, rotate at the same time through different angles.

We have also shown that the structure of these small crystals is the same as that of the original crystal. For this purpose an Ag line Röntgen spectrum was photographed from the plane (110) both of an unstrained and a strained crystal. Both spectra coincided: thus the constant of the crystalline grating did not alter. Similar results were obtained for calcium sulphate and also for a series of natural minerals with irregular faces. Quartz does not show any diffused spots until it breaks, its limits of elasticity and durability being the same.

The method of direct observation is a very convenient one for the determination of the limit of elasticity of different materials and also for the study of the manner of their destruction. Observations have shown, *e.g.*, that the durability of rock-salt depends not on the surface layer, as W. Voigt supposed, but only on the direction of the slide. Further "reversive" slides are observed at quite a definite amount of strain.

II. *The Elastic Strain.*

If we take two Laue röntgenograms on the same plate, the first from a plain crystal and the second from the same crystal under strain, we obtain double spots, and from the distances between those spots we can measure the angles through which different crystallographic faces rotate when strain is produced.

In order to measure the variation in the intra-atomic distances, we use a diverging beam of monochromatic Röntgen rays. The double picture produced from the normal and from the strained crystal shows in such a case the variation of the grating constant. The monochromatic rays were produced by a tube with a silver or a molybdenum anticathode with a filter of 0·006 mm. thickness of palladium or niobium respectively in the path of the rays. Under these conditions and with voltages less than 40 k.v. the K_α radiation contains about 98 per cent. of the energy of the beam.

The method we use has the advantage that on two photographs strains in every direction are obtained and all the constants of elasticity determined on one small sample of the crystal.

Röntgenological and Radiological
Institute, Petrograd.
1919.

XIX. *On a Graphical Solution of a Class of Differential Equations occurring in Wireless Telegraphy.* *By* ALFRED A. ROBB, *Sc.D., F.R.S.; with Note by* E. V. APPLETON, *M.A.*[*]

PART I.

THE differential equations which we propose to consider are of the general form

$$\frac{d^2V_1}{dt^2}+f(V_1)\frac{dV_1}{dt}+m^2V_1=0. \quad . \quad . \quad . \quad (1)$$

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[*] Communicated by the Authors.

Such equations occur in the theory of the production of sustained electrical oscillations by various types of generators, such as the Poulsen and Duddell arcs, and the Dynatron, or the ordinary type of three-electrode thermionic tube.

If we put $t=\frac{\omega}{m}$ and write p instead of V_1, equation (1) takes the form

$$\frac{d^2p}{d\omega^2}+\frac{f(p)}{m}\frac{dp}{d\omega}+p=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which we shall take as the standard.

In order to obtain a solution of equation (2) we shall regard p and ω as the usual p and ω coordinates of a point on a curve; that is to say, p is to be taken as the length of the perpendicular from a fixed point on a tangent to the curve, and ω the angle which the perpendicular makes with a fixed line in the plane.

Now it is a well-known theorem in the differential calculus that

$$\frac{ds}{d\omega}=p+\frac{d^2p}{d\omega^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where s is the length of the arc of the curve measured from a fixed point in it.

Substituting in equation (2), we get

$$\frac{ds}{d\omega}+\frac{f(p)}{m}\frac{dp}{d\omega}=0,$$

which on integration gives

$$s+\frac{1}{m}\int f(p)dp=C, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where C is some constant.

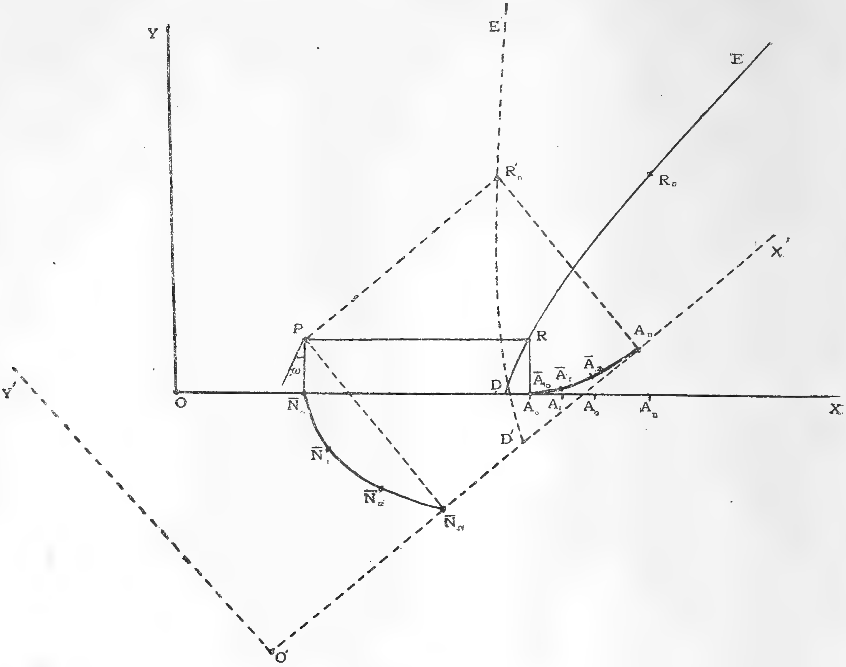
This is the p and s equation of any curve whose p and ω equation is a solution of the differential equation (2).

We have now to investigate a method of plotting such a curve.

Take a piece of transparent squared paper, (squared tracing paper), and taking rectangular axes OX and OY, plot on it in Cartesian coordinates the curve

$$x+\frac{1}{m}\int f(y)dy=C. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Let DE be the curve thus drawn.



Now take a plain sheet of paper fastened to a drawing-board and let a point P be marked on it with a dot.

Let the transparent squared paper be placed on the top of this, so that one of the lines on the squared paper parallel to OX passes through the point P, and let this line intersect the curve DE in the point R_0.

Let the perpendicular through P on OX meet OX in the point N_0, and let the perpendicular through R_0 on OX meet OX in the point A_0. Now let a pin-prick be made through N_0 into the lower paper, and let the point thus marked on the lower paper be denoted by $\bar{N}_0$.

Further, let a pin be stuck through A_0 into the drawing-board and let the point thus marked on the lower paper be denoted by $\bar{A}_0$.

Next let the squared paper be turned through a very small angle about the pin through A_0, so that another of the lines on it parallel to OX passes through the point P.

Let this line intersect the curve DE in the point R_1, which will be very near to R_0.

Let the perpendicular through P on OX in its new position meet OX in the point N_1, and let the perpendicular through R_1 on OX in its new position meet OX in the point A_1.

As before, let a pin-prick be made through N_1 into the lower paper and let the point thus marked on the lower paper be denoted by $\bar{N}_1$, and let a pin be stuck through A_1 into the drawing-board and let the point thus marked on the lower paper be denoted by $\bar{A}_1$.

The pin through A_0 is now to be removed and the squared paper turned through a very small angle about the pin through A_1.

Points N_2 and A_2 are now determined in a similar manner as were N_1 and A_1, a pin-prick made through N_2 into the lower paper and a pin stuck through A_2 into the drawing-board.

The points on the lower paper corresponding to N_2 and A_2 may now be denoted by $\bar{N}_2$ and A_2 respectively, and the process may be repeated an indefinite number of times.

We thus get two sets of pin-pricks in the lower paper :— $\bar{A}_0$, $\bar{A}_1$, $\bar{A}_2$, ... $\bar{A}_n$, and $\bar{N}_0$, $\bar{N}_1$, $\bar{N}_2$, ... $\bar{N}_n$; and the two broken lines $\bar{A}_0\bar{A}_1\bar{A}_2 \ldots \bar{A}_n$ and $\bar{N}_0\bar{N}_1\bar{N}_2 \ldots \bar{N}_n$ approximate indefinitely to two curved lines as we take the small angles of rotation of the squared paper more and more minute.

We shall call these the $\bar{A}$ curve and the $\bar{N}$ curve respectively.

Now, provided that the curvature of the $\bar{A}$ curve remains of one sign in a given stretch, it is evident that

$$\bar{A}_0\bar{A}_1+\bar{A}_1\bar{A}_2+\ldots+\bar{A}_{n-1}\bar{A}_n=A_0A_1+A_1A_2+\ldots+A_{n-1}A_n=A_0A_n.$$

If, however, in one part the curvature of the $\bar{A}$ curve is positive and in another negative, lengths must be taken with opposite signs along these two parts if this equation is to hold *.

With this understanding, we see that A_0A_n tends in the limit to the length of the $\bar{A}$ curve between the corresponding points.

Again, $P\bar{N}_0$, $P\bar{N}_1$, $P\bar{N}_2$ .... $P\bar{N}_n$ are the perpendiculars from P on the various positions of the line OX, which in the limit becomes the tangent to the $\bar{A}$ curve; and so PN_0, $P\bar{N}_1$, &c. become successive values of p.

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* It is easy to see that a maximum or minimum in x as a function of y will correspond to a point on the $\bar{A}$ curve where the curvature changes sign.

Further, since $\mathrm{PN}_n = \mathrm{R}_n\mathrm{A}_n$ it is evident that the relation (4) is satisfied and so the A curve is the curve we have been seeking.

On the other hand, the N curve is one whose *polar* equation with P as pole is a solution of the differential equation (2), and is more convenient in practice than the A curve.

The giving of different values to the constant of integration C has the effect of shifting the origin of coordinates on the squared paper along the axis of X, and, since this has no influence on the process of solution, we may take any value of C we like.

The position of the point P with respect to the curve DE is important, however, since different positions correspond to different solutions of equation (2).

If we desire to obtain a solution of the differential equation so as to satisfy given initial conditions, we may suppose that we have initially

$$p = p_0$$

$$\frac{dp}{d\omega} = \left(\frac{dp}{d\omega}\right)_0.$$

Now in the usual method of deducing equation (3) given in books on the differential calculus, it is shown that the intercept between the point of contact A_0 and the foot N_0 of the perpendicular from P on the tangent at A_0 is equal to the value of $\frac{dp}{d\omega}$ at this point.

But this intercept is equal to $\mathrm{R}_0\mathrm{P}$ and so we have only to take an ordinate $\mathrm{A}_0\mathrm{R}_0$ equal to p_0 on the curve on the squared paper and measure off a length $\mathrm{R}_0\mathrm{P}$ equal to $\left(\frac{dp}{d\omega}\right)_0$ along a line parallel to the axis of x, in order to adjust the squared paper over the dot so as to give the required solution.

PART II.

By a slight modification of the method already described, it is possible to obtain a solution of the more general type of differential equation

$$\frac{d^2\mathrm{V}_1}{dt^2} + f(\mathrm{V}_1)\frac{d\mathrm{V}_1}{dt} + m^2\mathrm{V}_1 = \phi(t). \quad . \quad . \quad . \quad (1)$$

Equations of this form also occur in problems connected with wireless telegraphy and, in practically important cases, we generally, though not always, have

$$\phi(t) = a \sin mt.$$

In order to solve equation (1) we shall, as before, put $t=\frac{\omega}{m}$ and shall write p in place of V_1. Equation (1) then becomes

$$\frac{d^2p}{d\omega^2}+\frac{f(p)}{m}\frac{dp}{d\omega}+p=\frac{1}{m^2}\phi\left(\frac{\omega}{m}\right). \quad . \quad . \quad . \quad (2)$$

We shall, as in the former case, regard p as the perpendicular distance from a fixed point on a tangent to a curve, and ω as the angle which the perpendicular makes with a fixed line in the plane of the curve.

Then

$$\frac{ds}{d\omega}=p+\frac{d^2p}{d\omega^2},$$

where s is the length of the curve measured from a fixed point in it.

Equation (2) thus becomes

$$\frac{ds}{d\omega}-\frac{1}{m^2}\phi\left(\frac{\omega}{m}\right)+\frac{f(p)}{m}\frac{dp}{d\omega}=0\,;$$

which on integration gives

$$s-\frac{1}{m^2}\int\phi\left(\frac{\omega}{m}\right)d\omega+\frac{1}{m}\int f(p)dp=C, \quad . \quad . \quad . \quad (3)$$

where C is some constant.

We now take a piece of transparent squared paper and, taking rectangular axes OX and OY, we plot on it in Cartesian coordinates the curve

$$x+\frac{1}{m}\int f(y)dy=C. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Let DE be the curve thus drawn. We next take a plain sheet of paper fastened to a drawing-board and mark a point P on it with a dot.

Having selected a particular direction on the plain sheet of paper with respect to which the angle ω is to be measured, and taking P as pole, we plot upon it in polar coordinates the curve

$$r=-\frac{1}{m^2}\int\phi\left(\frac{\omega}{m}\right)d\omega. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

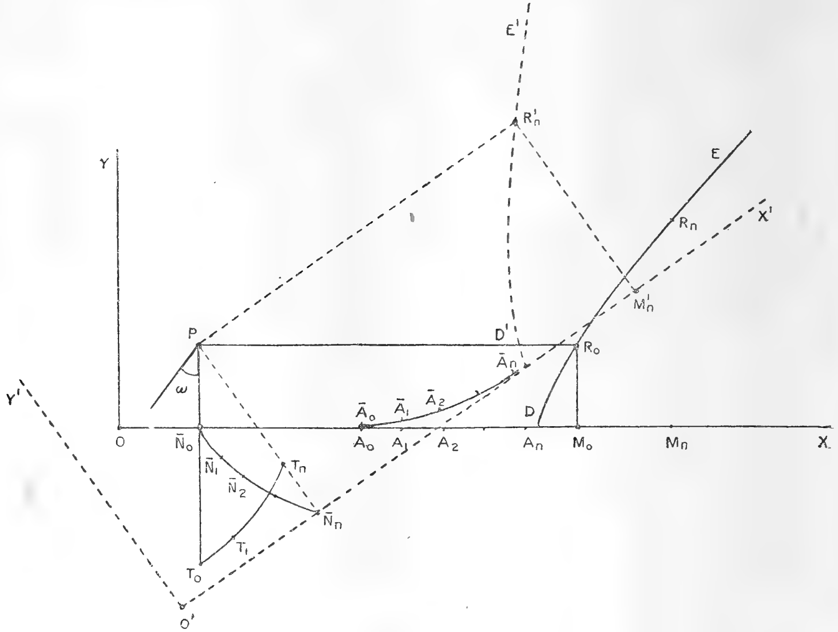
The constant of integration may be given any value we please, but it is convenient to give such a value as may render the curve as simple as possible.

P 2

We shall then have

$$s+r+\frac{1}{m}\int f(p)dp=\mathrm{C}.$$

Let the transparent squared paper now be placed on the top of the plain sheet so that one of the lines on the squared paper parallel to OX passes through the point P and let this line intersect the curve DE in the point R_0.



Let the perpendicular through P on OX intersect OX in N_0 and the curve (5) in T_0, and let the perpendicular through R_0 on OX intersect OX in M_0.

Let a length $\mathrm{M}_0\mathrm{A}_0$ equal to PT_0 (or r_0) be measured off along the axis of x, and let it be measured from M_0 in the negative direction if r_0 be positive, or in the positive direction if r_0 be negative; and let a pin be stuck through A_0 into the drawing-board.

Let the point of the lower paper thus marked be denoted by $\bar{\mathrm{A}}_0$.

Further, let a pin-prick be made through N_0 into the lower paper and let the point of it thus marked be denoted by $\bar{\mathrm{N}}_0$.

Next let the squared paper be turned through a very small angle about the pin through A_0 until another of the lines on it parallel to OX passes through the point P.

Let this line intersect the curve DE in the point R_1 which will be very near to R_0.

Let the perpendicular through P on OX in its new position intersect OX in N_1 and the curve (5) in T_1, and let the perpendicular through R_1 on OX in its new position intersect OX in M_1.

Let a length M_1A_1 equal to PT_1 (or r_1) be measured off along the axis of x as before and let a pin be stuck through A_1 into the drawing-board and the pin through A_0 be removed.

Let the point of the lower paper marked by the pin through A_1 be denoted by $\bar{A}_1$.

Also let a pin-prick be made through N_1 into the lower paper and let the point of it thus marked be denoted by $\bar{N}_1$.

Let the process, as described, be repeated an indefinite number of times and we obtain two sets of pin-pricks in the lower paper, $\bar{A}_0, \bar{A}_1, \bar{A}_2, \ldots. \bar{A}_n$ and $\bar{N}_0, \bar{N}_1, \bar{N}_2, \ldots. \bar{N}_n$, and these approximate indefinitely to two curved lines as we take the small angles of rotation of the squared paper more and more minute. We shall call these two curved lines the $\bar{A}$ curve and the $\bar{N}$ curve respectively.

It is evident that

$$\bar{A}_0\bar{A}_1+\bar{A}_1\bar{A}_2+\ldots.+\bar{A}_{n-1}\bar{A}_n=A_0A_1+A_1A_2+\ldots.\\+A_{n-1}A_n$$

and, if the $\bar{A}$ curve has its curvature of one sign in the interval, then this $=A_0A_n$ so that A_0A_n tends in the limit to the length of the stretch of the $\bar{A}$ curve.

Also $P\bar{N}_0$, $P\bar{N}_1$, $P\bar{N}_2, \ldots. P\bar{N}_n$ are the perpendiculars from P on the various positions of the line OX which in the limit becomes the tangent to the $\bar{A}$ curve; so that $P\bar{N}_0$, $P\bar{N}_1$, $P\bar{N}_2, \ldots. P\bar{N}_n$ become successive values of p for this curve.

Until we have shown that the $\bar{A}$ curve is the one required we shall distinguish the p and s of this curve by accents.

Now we have

$$P\bar{N}_n=R_nM_n,$$

and this is the ordinate of the curve (4) corresponding to the point M_n on the axis of x, while

$$A_0A_n+A_nM_n=A_0M_n$$

$$=OM_n-OA_0,$$

or

$$\bar{A}_0\bar{A}_n+r_0=x-OA_0.$$

Thus since $\bar{A}_0\bar{A}_n=\delta s'$, we have for the $\bar{A}$ curve

$$\delta s'-\frac{1}{m^2}\int\phi\left(\frac{\omega}{m}\right)d\omega+\frac{1}{m}\int f(p')dp'=x+\frac{1}{m}\int f(y)dy-OA_0.$$

But the right-hand side of this equation is constant, and so for the $\bar{A}$ curve, the relation (3) holds.

It is thus evident that the $\bar{A}$ curve is one whose p and ω equation satisfies the differential equation (2).

On the other hand, the $\bar{N}$ curve is one whose polar equation with P as pole satisfies the differential equation (2), and this curve is more convenient than the $\bar{A}$ curve for giving the relation between p and ω directly.

In the special case where

$$\phi(t)=a\sin mt,$$

the curve (5) becomes

$$r=-\frac{a}{m^2}\int\sin\omega\,d\omega,$$

$$=\frac{a}{m^2}\cos\omega+\text{const.}$$

If the constant of integration be taken as zero, we get the simplest curve, which is

$$r=\frac{a}{m^2}\cos\omega.$$

This is clearly a circle passing through P and of which the diameter is $\frac{a}{m^2}$.

Thus in this particular case, which is one of special importance, the curve (5) is very easily drawn.

The curve (5) might be drawn with a different pole from P in case we desire that it should not be in too close proximity to the $\bar{N}$ curve.

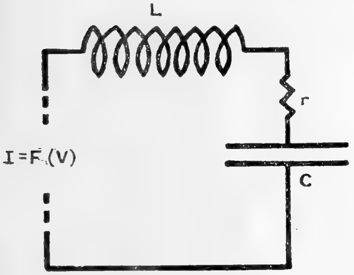
The lines on the squared paper parallel to the axis of y would still give the proper direction of the radius vector.

It will be observed that if the function ϕ is zero the points A_0, A_1, A_2, ... A_n coincide respectively with the points M_0, M_1, M_2, ... M_n and we get the same result as previously obtained.

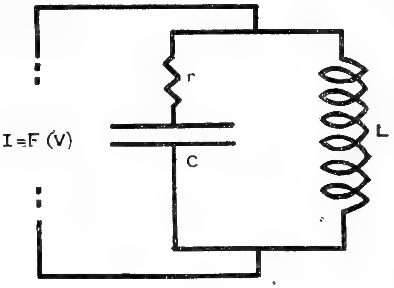
In conclusion, I wish to express my best thanks to Mr. E. V. Appleton, who called my attention to the importance of this problem.

Note on the above by E. V. Appleton, *M.A.*

The production of undamped electrical oscillations is nowadays accomplished in various ways. But in most cases the assembly of the generator may very simply be reduced to two elements, (1) an oscillatory circuit containing self-inductance, capacity, and small resistance, and (2) some type of conductor possessing a non-linear voltage-current characteristic. Sometimes the conductor is placed in series with the capacity in the oscillatory circuit as in the Poulsen arc, but more often it is included as a shunt across the condenser as in the Dynatron* and the ordinary triode generator†. (See accompanying figures where the conductor is shown as possessing a characteristic current-voltage relation I=F(V).)



Arc



Dynatron or Triode

In either case the fundamental equation of the generator representing the relation between the voltage V_1 across the condenser, and time t, may be reduced to

$$\frac{d^2V_1}{dt^2}+f(V_1)\frac{dV_1}{dt}+m^2V_1=0, \quad . \quad . \quad . \quad . \qquad (1)$$

where $f(V_1)$ and m^2 include the circuit constants C, r, and L. For many purposes it is sufficient to consider the characteristic I=F(V) as linear (*e.g.* in deducing the limiting conditions for instability), but it is clear that the inclusion of the non-linear terms is essential in a discussion of the maintained amplitude of the oscillations or the production of harmonics.

A certain amount of progress towards the solution of (1) for the somewhat limited cases in which $f(V_1)$ may be simply expressed as a power series has been made by Dr. van der Pol and the writer ‡, but no extension has been made to the case where the right-hand side of the equation is not zero. The latter case (dealt with in Part II. of Dr. Robb's paper) is of practical importance as representing the case of a sinusoidal electromotive force impressed on a crystal or triode receiver circuit.

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* Hull, Proc. Rad. Inst. Eng. vol. vi. p. 5 (1918).

† Appleton and van der Pol, Phil. Mag. vol. xlii. p. 201 (Aug. 1921).

‡ Phil. Mag. *suprà*, p. 177.

XX. *On Certain Types of Electric Discharge.* *By* Prof. D. N. Mallik, *F.R.S.E.*, *and* Prof. A. B. Das, *M.Sc.*[*]

1. IN previous papers (Phil. Mag. Oct. 1908, Oct. 1912, July 1916) we studied the behaviour of electric discharge in a De La Rive tube, under gradually decreasing pressure. In the present series of experiments, tubes of ordinary pattern (with electrodes consisting of thin rods) were used, in order to verify the various theoretical deductions, previously arrived at.

2. Three tubes ($T_1=34\cdot4$ cm. in length, $T_2=14\cdot5$ cm., and $T_3=4\cdot2$ cm.) were used in parallel, in order that the effects of length and decreased pressure on the character of the discharge should be clearly observable. The induction-coil used gave a spark-length of 19·94 cm. in air, with a spherical electrode of 3 cm. in diameter.

3. At a pressure of 73 mm. no discharge passes in T_1, it is spindle-shaped in T_2 while in T_3 it is in the form of a band. As the pressure is further reduced at 20·5 mm. the discharge in T_1 is spindle-shaped, T_2 shows a band which was the stage reached in T_3 at the higher pressure, while in T_3 the band is changing into a glow discharge.

4. On the theory previously worked out, the spindle-shape is due to the mutual repulsion between the various streams of discharge, which is seen to be operative, in spite of the symmetry of the electrodes.

5. Moreover, during the band stage, according to theory previously worked out, the result of ionization is annulled by recombination. Now ionization depends on $\frac{X}{p}$, where X is the electric intensity along the discharge and p the pressure. This quantity, therefore, depends on $\frac{1}{lp}$ where l is the length of the tube. The effect of decreasing the length must, therefore, correspond to that of increasing the pressure. As, however, the potential difference itself depends on length and pressure (arts. 15 and 16), there is not as yet sufficient material for working out the law of this correspondence.

6. It is found that it is only when the discharge is in the form of a thin band or a single stream of discharge, that there is an action (attraction or repulsion) when the discharge-tube is placed in a transverse magnetic field. In the actual experiment, a rectangular coil of wire, carrying current, two

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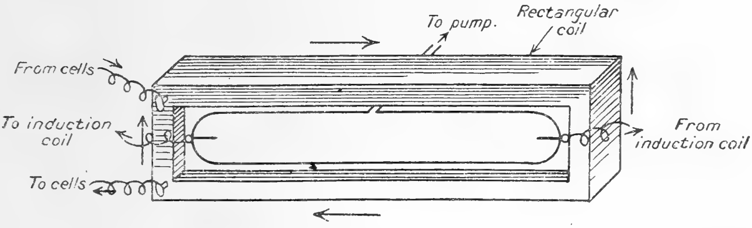
[*] Communicated by the Authors.

of whose sides are parallel to the tube, was used to produce such a field, fig. 1.

Fig. 1.



7. According to the theory previously worked out, this usual electrodynamic action between currents will be observable only when the discharge is in the form of a band, the number of corpuscles in this case being equal to that of positive ions.

The present experiment, therefore, is in confirmation of this theory.

8. When the pressure is further reduced (·03 mm.) T_1 shows fine striatory discharge.

This tube thus does not at all show the band stage—which alone is affected by a magnetic field—with the induction-coil used in the above experiment.

9. At this pressure, the discharge in T_2 is striatory but the striæ are thicker ; while in T_3 the positive column is entirely absent, the cathode glow extending over the whole length of the tube.

10. It will be seen that the characteristic changes in these discharge-tubes and the characteristic differences between the three tubes arising from a difference in length correspond to the peculiarities exhibited by the curves connecting pressure and potential difference in them.

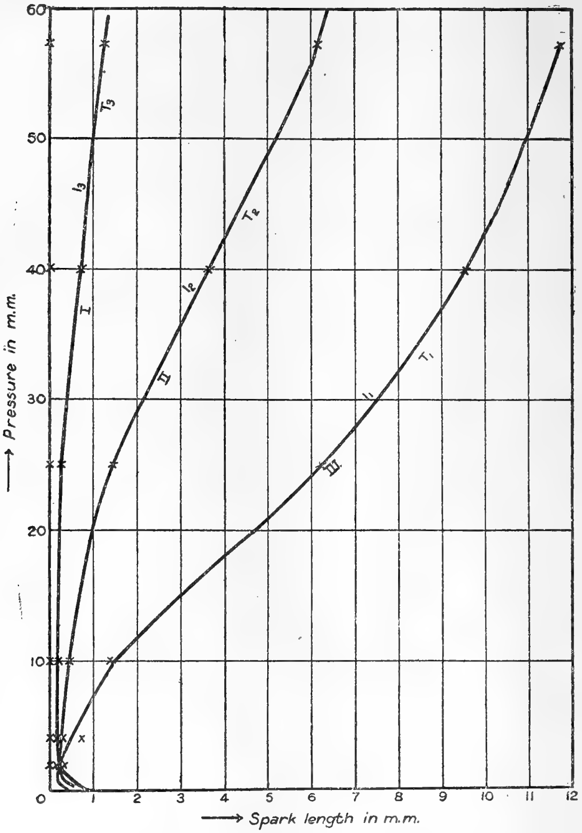
Curve II, fig. 2, gives the relation between pressure and potential difference in T_2.

11. In T_2, at high pressure down to nearly 55 cm., the showery stage is indicated by the curved line. From this pressure to nearly 25 cm., the discharge is in the form of a band. This is indicated by a straight portion in the curve. The discharge behaves during this stage as an ordinary flexible wire carrying current. As the pressure is further reduced, the curve bends away from the line of pressure, the difference of potential increasing enormously with decreased pressure, when the pressure is lowered below 2 mm.

In the case of T_3, the first stage is absent, as well as the first portion of the curve. (Curve I, fig. 2.)

In T_1 the second stage is absent, and the second portion of the curve with it. (Curve III, fig. 2.)

Fig. 2.



Spark-length of the induction-coil = 19·94 mm.

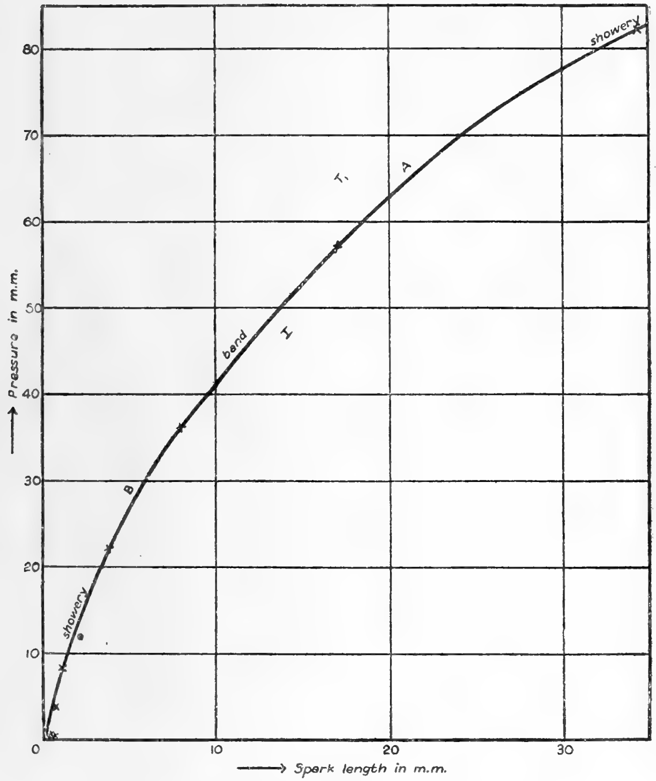
12. When, however, the voltage of the induction-coil is increased, the discharge in T_1 also passes through all the various stages and the curve I (fig. 3) exhibits the usual peculiarities in their entirety.

13. These characteristics are the same as those exhibited by De La Rive tubes. They are, therefore, common to all electric discharges, as they should be on theoretical grounds.

14. It is possible to work out an approximate theory giving a relation between pressure, potential difference, and the length of the discharge-tube, but the formula

obtained is much too complicated for discussion to serve any useful purpose, at the present stage.

Fig. 3.



Spark-length of the induction-coil=46 mm.

15. In the particular case in which the curve is a straight line, the formula obtained in a previous paper was

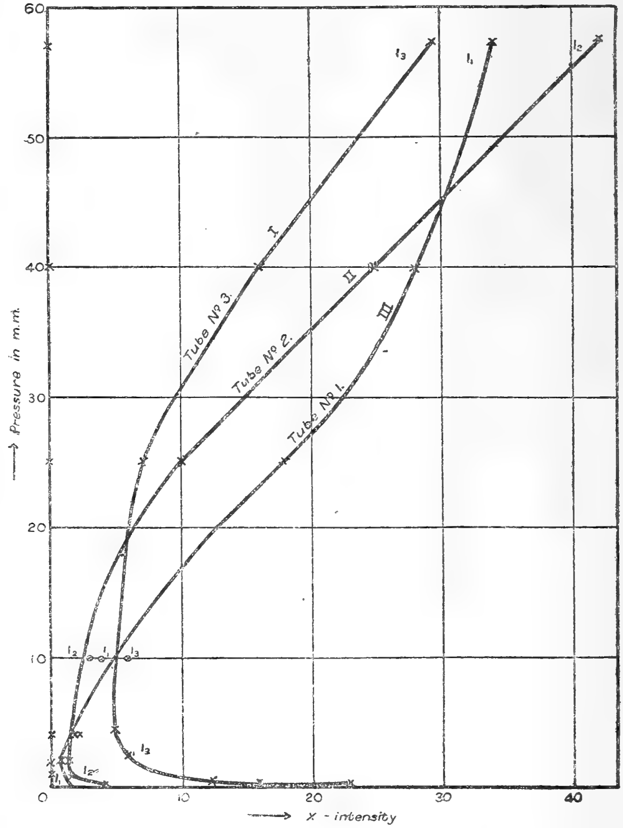
$$V_0 = \frac{X}{p} \cdot \frac{q + q'\frac{\lambda'}{\lambda}}{q+q'},$$

where V_0 is the difference of potential between the terminals of the induction-coil *when the circuit is open*, X' the electric intensity, assumed to be constant throughout the tube, q, q', velocities of +ions and corpuscles, and λ, λ', their mean free paths, p being the pressure.

16. Now experiment shows that X itself depends on the

discharge circuit, at any rate with an ordinary induction-coil provided with a metallic interrupter, which is controlled by a spring. Thus, with such an induction-coil of spark-length in air equal to about 20 mm., when the discharge was passed through the tube T_1, the interrupter worked with much greater frequency than when the tube T_3 was in circuit. This is verified, by the curves I and II, fig. 4.

Fig. 4.



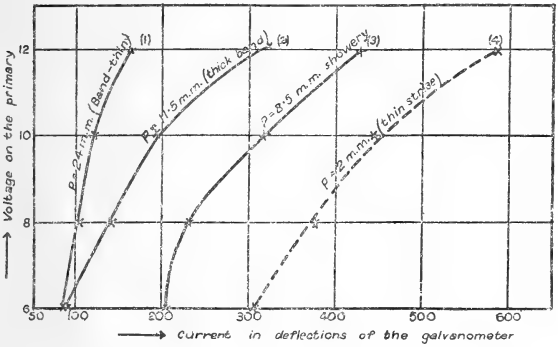
X = *f*(*p*). If in the above formula X were independent of the discharge-tube, the straight portions of the two curves ought to have been nearly coincident, if, at any rate, we could admit $q\propto\frac{1}{l}$, $q'\propto\frac{1}{l}$, $\lambda\propto\frac{1}{l}$, $\lambda'\propto\frac{1}{l}$.

17. The interdependence of the various factors that enter into the phenomena is clearly brought out by the curves 1,

2, 3, 4 (fig. 5). Thus, it is seen that for the same E.M.F. in the primary, the current as well as the character of the discharge depend on the pressure.

There is one feature of this phenomenon brought out by these curves, which is worthy of notice. When the discharge is in the form of a band (curve 1, fig. 5) (pressure 24 mm.) within a certain range, the current is proportional to the E.M.F. of the primary. Now, according to Ohm's law, the current in a wire circuit is proportional to the E.M.F. when the *circuit* is *open*. As we may reasonably take the E.M.F. of the secondary, when no discharge passes, proportional to the E.M.F. in the primary, we conclude that the band discharge satisfies the criterion of a current in a wire circuit, in respect of Ohm's law. This is of interest in view of art. 6.

Fig. 5.



18. When the striatory discharge (in tube T_2) is placed in the centre of a rectangular coil carrying current, the number of striæ increases, and in the actual experiment they become inclined to their original directions, while as the current is reversed, the inclination is reversed also.

19. A tentative theory of these experimental results (art. 18) may be given as follows:—

The Faraday dark space is, as we have seen ("Electric Discharge in a Transverse Magnetic Field," Philosophical Magazine, July 1916), a region practically devoid of ions. If this is so, all the dark spaces in the striatory column must be held to be also regions containing but few ions, and *per contra*, the illuminated portions to mark regions where there is copious ionization.

20. A corpuscle being thrown off from the negative electrodes will be in a condition to ionize the gas almost directly, if the pressure of the gas in the tube is sufficiently

high; for the electric intensity near the cathode, in this case, being great, the energy required by a corpuscle for ionizing the gas will be acquired at once.

21. As the pressure decreases, the electric intensity near the cathode decreases also, and the corpuscle has to move through a finite distance under the action of the electric force before it acquires sufficient energy for producing ionization. The space through which a corpuscle shot off from the cathode has to traverse, before it is in a condition to ionize the gas, would be the Faraday dark space. The energy so acquired, however, is used up in producing ionization in the first illuminated area. A corpuscle issuing from this illuminated area has, therefore, to move through some distance before it is again in a condition to ionize the gas. But as the average electric force at the striæ is greater than along the Faraday dark space (H. A. Wilson, Proc. Camb. Phil. Soc. xi.) a corpuscle has to move through a much shorter distance than the Faraday dark space, in order to recover the minimum energy required (Phil. Mag. Feb. 1920) for ionization. Accordingly, the dark space along the striæ is of shorter length than the Faraday dark space.

22. When a radial magnetic field is introduced, a corpuscle issuing from the cathode tends to move under the electric force along a line of discharge and undergoes at the same time an angular displacement under the magnetic force. The resultant velocity acquired attains to the minimum value required for ionization at a shorter distance from the cathode than when the magnetic field was not on. The effect of a magnetic field is, therefore, to *shorten the Faraday dark space and all the other dark spaces and*, pari passu, *to increase the number of striæ*. Moreover, the ions in the striatory discharge, under the joint effect of electric and magnetic fields, move in a *spiral*, the tangent to the spiral at any point being inclined to the axis of the tube, one way or the other, according to the direction of the magnetic lines of force in the field. Remembering that the movement of ions under the electric field itself produces a magnetic field (necessarily comparatively weak in comparison with the extraneous field that may be introduced), we conclude that ions in a striatory discharge in general move in spirals, more or less inclined to the axis of the tube, even without the application of a magnetic field.

Measurements are being undertaken for a quantitative verification of the above theory.

Our thanks are due to the authorities of the Presidency College, Calcutta, for facilities for carrying on our work there.

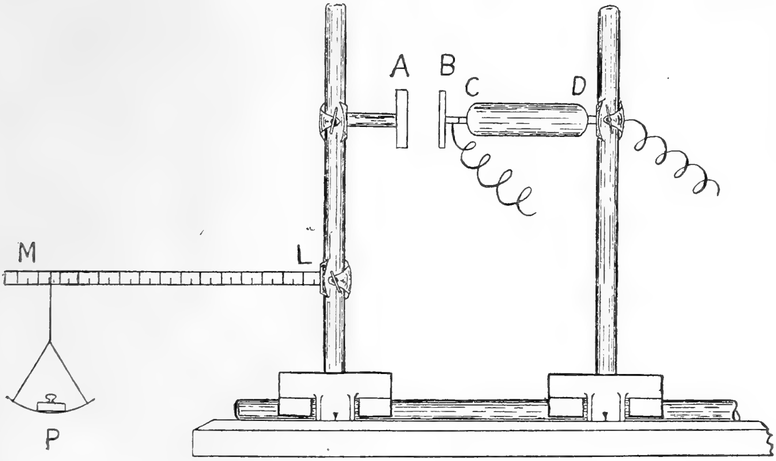
XXI. *The Application of the Ultra-Micrometer to the Measurement of Small Increments of Temperature.*

By W. Sucksmith, *B.Sc., University of Leeds*[*].

IN Whiddington's ultra-micrometer apparatus[†] two oscillating valve circuits were set up. In the valve-anode circuit of the second was inserted a three-stage amplifier, together with a loud-speaking telephone, to magnify suitably the heterodyne note produced. The condenser in the first oscillating circuit consisted of two parallel plates, the variations in the distance of which produced variations in the note emitted from the telephone. A tuning-fork was set up close to a small telephone, in order to provide a standard of pitch to which the note from the interfering circuits could be adjusted. The oscillations of this fork are amplified into the loud-speaking telephone mentioned above.

This differed from the original experiment in that previously a third oscillating valve circuit had been set up inducing into an amplifier, with capacity and inductances so large as to produce an audible note in the telephone.

Fig. 1.



The method used was to attach a metal bar to one of the condenser plates, and measure change in the temperature by the change in the note produced in the telephone.

Fig. 1 shows a geometrical slide carrying two rigid vertical

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[*] Communicated by Prof. R. Whiddington, M.A., D.Sc.

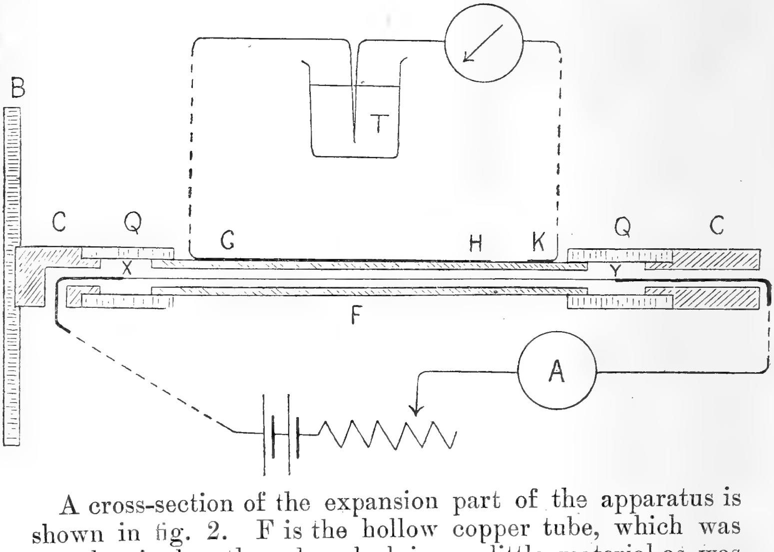
[†] Whiddington, "The Ultra-Micrometer," Phil. Mag. ser. 6. vol. xl. pp. 634–9.

rods. To the left-hand one is attached a polished steel condenser-plate A, 17 sq. cm. in area and about 5 mm. thick, and insulated from the supporting rod by a thin sheet of mica. The distance separating the two condenser-plates can be varied by a bending couple applied by placing weights in the pan K which hangs from the graduated quartz rod ML. The right-hand condenser-plate B is made of polished aluminium 2 mm. thick, and is rigidly attached to the end of the copper rod CD (which is shown enclosed in non-conducting materials) the change in temperature of which is to be measured.

The method is as follows. Initially the scale-pan P is empty. The heterodyne note in the telephone is adjusted by means of an auxiliary condenser in the second circuit to be within 2 beats per second of the note produced by the fork. The copper rod, which is hollow, is heated electrically, thus bringing the aluminium plate B nearer to A. Weights are then placed in the pan until the same number of beats as before are heard in the telephone.

A knowledge of the weight required to produce a certain lateral shift of the plate A, together with the expansion coefficient of the specimen of copper used, enables the rise of temperature to be determined.

Fig. 2.



A cross-section of the expansion part of the apparatus is shown in fig. 2. F is the hollow copper tube, which was 4 inches in length and embodying as little material as was consistent with rigidity. Two pieces of quartz Q Q were fitted tightly over the ends of this tube. Inside the ends of the quartz tube were fitted short lengths of invar C C, drilled as shown to admit the leads connected to the heating wire XY. Hard-setting sealing-wax was used to make the joints tight.

The heating wire XY was of constantan, soldered to thicker copper leads, and connected through a low-reading ammeter A and an adjustable rheostat to a battery. The whole of this wire was carefully insulated from the rest of the apparatus, the spaces between the quartz and the heating wire being plugged with cotton-wool to prevent convection currents.

The temperature of the copper was determined by a copper-constantan couple, which had been previously calibrated by an accurate thermometer. A constantan wire, C, soldered along the length of the copper tube, *i. e.* along GH, formed the hot junction. The cold junction was kept some distance away in a water-bath protected from air currents.

The thermo-couple leads were connected directly to a suitable galvanometer, the scale of which was so adjusted that ·01° C. difference of temperature between the junctions could be read easily.

A series of preliminary experiments were performed, and it was found that the rise in temperature of the copper tube followed the ordinary laws for increments up to 3° C., which was greater than required for the experiment. Further, the system maintained that temperature over an interval of time sufficient to allow the plate A to be readjusted. The heat equivalent of the system was found to be 3·74 calories per degree C.

To determine the lateral displacement of the plate A, produced by placing weights in the pan, the method used in the original experiment was repeated. Large bending moments were applied to the quartz rod, and the displacement measured by a micrometer, contact being indicated electrically.

It was found that 1·8 grams placed one inch along the rod displaced the centre of the rod 10^{-6} inch.

The copper tube was heated to exactly 1° C. above the cold junction. 15·3 grams were required to restore the note to that emitted by the fork. This gives the coefficient of linear expansion of the copper used as $\cdot 17 \times 10^{-4}$ per degree C., the actual expansion being $\cdot 68 \times 10^{-4}$ inches.

Thus the arrangement is capable of detecting a change of temperature of $\frac{4 \cdot 3 \times 10^{-9}}{68 \times 10^{-4}} = 000063^\circ$ C., or about $\frac{1}{16000}{}^\circ$ C., since the smallest distance measurable by the ultra-micrometer was $4{\cdot}3 \times 10^{-9}$ inch.

It was observed that whilst the heating current was flowing, the note emitted by the telephone changed very smoothly, showing that no discontinuity in expansion could be detected even with an apparatus capable of measuring $\frac{1}{200}$ millionth of an inch.

My grateful thanks are due to Professor Whiddington for suggesting the experiment and allowing me to use his original apparatus, and also for his advice during the work, which was carried out in the University Physics Laboratories.

Leeds University.

XXII. *An Interesting Case of Mechanical Disintegration caused by Positive Ions.* *By* H. P. WARAN, *M.A., Government of India Scholar of the University of Madras**.

WHILE studying the effect of a transverse magnetic field on the spectrum of an electric discharge through a rarefied gas, it occurred to the writer to examine the extent of the disintegration of the walls of the tube caused by the bombardment of ions deflected on to them by the magnetic field. An ordinary Plücker discharge-tube containing pure nitrogen at a few millimetres pressure was arranged with its capillary between the conical poles of an electromagnet, as shown in fig. 1, and excited by the unrectified current from the secondary of an induction coil.

It is easy to see that under the influence of the field transverse to the direction of the discharge, the discharge gets split into two streams, as shown in fig. 2, corresponding to the make and break currents which travel in opposite directions. Further, it is also evident that the corresponding ions in the two streams travel in opposite directions and get deflected to the opposite sides of the tube.

Ordinarily the current through the tube is about 2 m.a. and the field about 5000 C.G.S., and very little of any local disintegration opposite the pole-pieces is noted. But by screwing the break of the coil and increasing the current through the magnet coils it is possible to pass a heavy discharge of about 15 m.a. in a field of the order of 10,000 C.G.S. momentarily, thus intensifying the disintegration considerably. Under such circumstances, in a few seconds a grey streaky patch developed on either side of the walls of the capillary, indicating a corrosion of the glass under the

* Communicated by Prof. A. W. Porter, F.R.S.

Fig. 1.

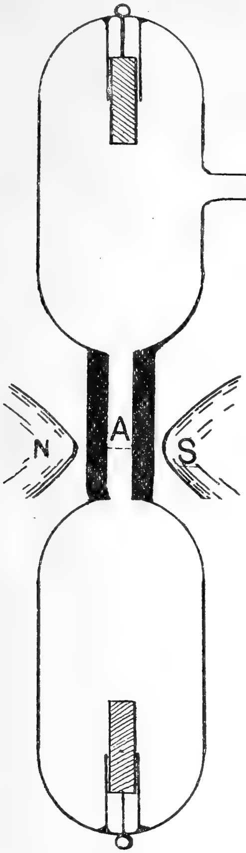
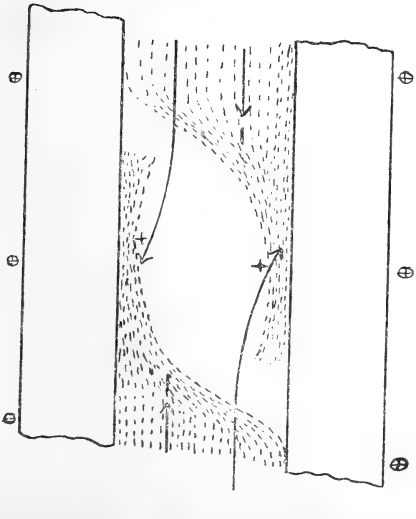
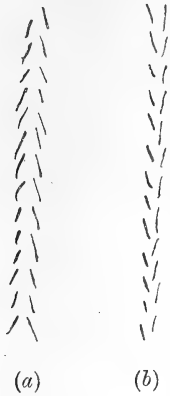


Fig. 2.



sand-blast action of the ions. This region, when examined with a low-power microscope, revealed the presence of a series of short little grooves cut into the glass, all converging in a direction parallel to the axis of the tube and presenting a pretty pattern, as illustrated in fig. 3 (*a*).

Fig. 3.

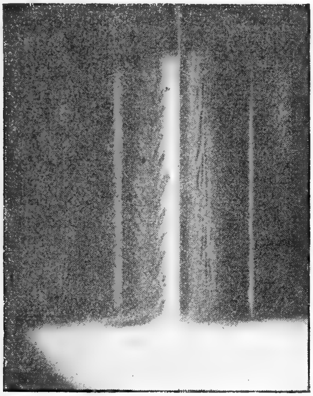


On examining the similar streak diametrically opposite, caused by the impact of ions from the reverse current, it was interesting to note that they all gave a pattern of grooves quite similar, as shown in fig. 3 (*b*), but with the grooves converging in a direction exactly opposite.

There can be very little doubt that this grooving of the glass was effected by the bombardment of the massive positive ions which travel in opposite directions in the two streams causing grooves that converge in opposite directions. A closer examination, taking into consideration the direction of the currents and the deflecting field, confirmed the truth of the above explanation. To make the point sure, with a point and plate in series with the tube the reverse current was practically cut off, and the corresponding streak disappeared accordingly. When the upper electrode was the cathode, and the lines of force passed from left to right, the grooving was found to be on the side away from the observer and converging upwards, as would be the case if the positive ions were the cause of this peculiar corrosion.

Fig. 4 is an enlarged view through the capillary of a discharge-tube in which the grooves have been formed, taken especially to show both the sets of grooves side by side converging in opposite directions.

Fig. 4.



The reasons why these grooves are on the average of about the same length and occur evenly spaced, start from about the same azimuth and converge, are other noteworthy points of special interest under further investigation.

University College, London.

XXIII. *The Relative Affinity of some Gas Molecules for Electrons.* By Leonard B. Loeb, *Ph.D., National Research Fellow, University of Chicago* *.

IN a recent paper the writer has shown that in some gases the electron must on the average make a number of impacts n with the molecules of the gas before it can strike one in such a manner as to attach to it to form the negative ion †. In this same paper it was also shown that this quantity n varied with the chemical nature of the gas. It consequently becomes of interest to determine the value of n for a number of the common gases. It is the purpose of this note to discuss briefly the bearing of a recent study of electronic mobilities in N_2 on the determination of this constant, and on the basis of this to evaluate n for a series of gases from the experimental measurements made by the writer and Mr. Wahlin.

* Communicated by Prof. R. A. Millikan.

† L. B. Loeb, Phys. Rev. xvii. No. 2, pp. 89–115 (Feb. 1921); Proc. Nat. Acad. Sci. vii. No. 1 (Jan. 1921).

It has been shown * that the current i between two condenser plates as a function of the alternating potential difference V between them when one of them is illuminated by ultra-violet light is represented by the equation

$$\frac{i}{i_0} = e^{-\frac{W}{nK'\lambda'}\left\{\frac{d^2\left(\frac{p}{760}\right)^2}{V} - \frac{K\left(\frac{p}{760}\right)}{N}\right\}} \quad . \quad . \quad . \quad . \quad (1)$$

with a fair degree of approximation. In this equation p is the pressure of the gas in mm., V is the alternating potential difference of square wave-form in volts, d is the plate distance, N is the frequency of alternation, K is the mobility of the negative ions at 760 mm., K' is the electronic mobility, λ' the mean free path of the electron at 760 mm., W the energy of thermal agitation of the electron, i/i_0 the fraction of the maximum current possible existing under the given conditions, and n the constant of attachment. It was also shown that if the mobility of the electron K' be assumed equal to 200 † cm./sec. volt/cm., and if it be assumed that the mean free path of the electron is $4\sqrt{2}$ of that of the gas molecules, then by inserting the value of W, the velocity of thermal agitation of the electron, into the equation, it became capable of experimental verification in the form

$$\frac{i}{i_0} = e^{-\frac{1{\cdot}08\times10_9}{n}\left\{\frac{d2\left(\frac{p}{760}\right)^2}{V} - \frac{K\left(\frac{p}{760}\right)}{N}\right\}} ; \quad . \quad . \quad . \quad (2)$$

n may be evaluated by choosing a point near the feet of one of the current-voltage curves and placing the values of the various quantities into the equation above. The n so obtained was found to be constant in *order of magnitude* for a considerable range of pressures and frequencies for any given gas ; in fact, n for oxygen was found to lie between 2×10^4 and 3×10^5 in gases which varied in oxygen content from that of pure oxygen to a mixture of 745 parts of nitrogen to one part of oxygen. The range of pressures covered in this set of determinations varied from 15 mm. to 750 mm., while N varied from 70 alternations per second to 750 alternations.

This variation in n between 2×10^4 and 3×10^5 seems to be a definite variation in n with some of the experimental

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* L. B. Loeb, *loc. cit.*

† This was the most reliable value of electronic mobility in nitrogen available at the time of publication of the original paper.

factors. In general it was observed that for a set of curves taken at different pressures and frequencies, the values of n were uniformly greater the lower the pressure. However, the parts of the curves from which n was taken under these conditions also lay at progressively lower values of the voltage as the values of n increased. It was therefore *a priori* difficult to determine which of the variables, if either, was responsible for the changes in n. As has been pointed out before, this variation in n does not necessarily invalidate the theory of electron attachment which assumes n to be a constant; for the change in n may be only *apparent*. A real change in K′ of the equation (1) (about whose behaviour little is known) could be the real cause of the variation.

In the hope of gaining some insight into this situation, the values of n were determined for mixtures of oxygen and nitrogen. It was found that as the nitrogen became very pure the value of K, the mobility of the carriers, became quite large. In pure nitrogen, values of K were obtained of the order of 1100 cm./sec. It was further found that the variation in n due to pressure observed when the quantities of oxygen were small, was greater than with air or pure oxygen. For example, it was found that in order to change n from 1×10^5 to 9×10^5 in air the pressure-change required was from 150 mm. down to 20 mm. In a mixture of 1 mm. oxygen to 745 mm. nitrogen it required a change from 508 mm. to 222 mm. to cause a change in n (computed back to air) of from $1{\cdot}0 \times 10^5$ to $1{\cdot}5 \times 10^6$. The change of n with the voltage was about the same in the two cases. The effect is then obviously not produced by a variation in the pressure alone, and is perhaps influenced by the value of the field strength.

An investigation of the electronic mobilities became imperative, in view of the fact that measurements had revealed negative carriers in pure nitrogen whose mobility was five times as great as those assumed for K′, from the work of earlier observers[*]. The mobilities of electrons in pure nitrogen gas were determined, using high-frequency oscillations from an audion oscillator These results are being published elsewhere[†]. The measurements showed that the mobility of the electron in nitrogen was far higher than had been anticipated. It was further found that K′ was not

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[*] J. Franck, *Verh. d. Deut. Phys. Ges.* xii. p. 613 (1913); W. B. Haines, Phil. Mag. (6) xxx. p. 503 (1915); E. M. Wellisch, Am. Journ. Sci. July 1917, p. 11.

[†] To appear in the Physical Review, 1921.

a constant, but that it varied according to the equation

$$K = \frac{571,000}{21 + 760V/pd} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here V is the voltage, p is the pressure in mm., and d is the plate distance. This result at first sight seems strange. Townsend[*], however, had pointed out that for electrons making elastic collisions with gas molecules W, the velocity of the electrons among the gas molecules, must increase as a function of the field strength. If this occurs the mobility K' of the electron will, according to him, decrease as the field increases. These results obtained on electrons in N_2 show that it is possible to ascribe the apparent variations in n to real variations in K'; for they show that K' does in one instance vary as a function of the pressure and the field. It is very doubtful whether the above results in N_2 may be rigorously carried over to other gases for the purpose of evaluating n. Since, however, K' has been shown to be a function of V/d, and of p, it is certain that in comparing the values of n for different gases, these values of n must be chosen from data for which the field strength and the pressure are as nearly the same as possible. In determining the values of n to be used in the table, care has been taken to choose values obtained when the field strength is close to 20 volts per cm. and the pressure is as near 75 mm. as practicable.

In the recent work on the mobility of electrons in nitrogen it was found that the value of K' at a field strength of 20 volts/cm. and a pressure of 75 mm. lies close to 2800 cm./sec. This requires that the absolute values of n heretofore determined on the basis of $K'=200$ must be modified. Furthermore, it is obvious that in order to apply the equation to the evaluation of n in other gases, where the value of K' is not known at all, some tentative value of K' must be assumed. It is known that the mobility of the negative ion in different gases does vary by small amounts. In the evaluation of n from these experiments the value of K' for the electrons in the different gases will be taken as the value of the electron mobility in N_2 (*e. g.* 2800 cm./sec.) multiplied by the ratios of the mobilities of the *negative ions* in the gas to the mobilities of *negative ions* in N_2 (*i. e.* $K' \text{gas} = K'_{N_2} \frac{K \text{ gas}}{K_{N_2}}$, where K represents the *ionic* mobilities). The values of n, the constant of attachment

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[*] J. S. Townsend, Elect. in Gases, p. 124 (Oxford, 1914); Phil. Mag. (6) xl. p. 505 (1920).

of electrons given in column 4 of the table, were calculated on the basis of equation (1), using values of K′ estimated in the manner suggested above *.

If the equation of electron mobility suggested by Townsend † be accepted as correct it becomes evident that one is not justified in computing n according to the equation (1); for in Townsend's equation the velocity of agitation of the electron among the gas molecules is not a constant. Also, if from the view-point of this equation the value of λ' be computed from the results of the electron mobility measurements in N_2, a value of λ' which is several times greater than that estimated on the basis of kinetic theory results. The uncertain quantities λ' and W may be eliminated from the equation by substituting the value of W/λ' obtained from the Townsend equation,

$$300\,K' = \frac{\cdot 815\, e\lambda'}{mW},$$

in equation (1). In this equation e is the electronic charge, m is the mass of the electron, and the factor 300 is put in to reduce the mobilities to volts per cm. The equation (1) then becomes

$$\frac{i}{i_0} = e^{-\frac{\cdot 815\, e}{300\, nm(K')^2}\left\{\frac{d^2\left(\frac{p}{760}\right)^2}{V} - \frac{K\left(\frac{p}{760}\right)}{N}\right\}} \quad . \quad . \quad . \quad . \quad (4)$$

The factor K′ is then the only uncertain factor present in the equation besides the n which is to be determined. In the table of results the values of n computed on the basis of this equation are given in column 2.

The preparation and purification of air, N_2, O_2, and H_2, used in the determinations has been reported elsewhere ‡. The CO_2 was prepared through the action of HCl on pure marble. It was passed through a tube packed with $NaHCO_3$, then over heated CuO, and heated, finely divided, Cu. From there it passed through a drying train of $CaCl_2$ and P_2O_5 tubes into the chamber through a trap cooled to $-20°$ C. by frozen CCl_4. Absorption tests made with $CaCl_2$ failed to reveal the presence of any water-vapour. On absorbing the CO_2 in NaOH a residue of 1 c.c. of an inert gas was found present in about 250 c.c. of the gas. Tests with alkaline pyrogallol indicated that this residue was free from oxygen.

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* This changes the value of N for O_2 to $3\cdot 6 \times 10^3$ instead of 50,000 given in the original paper.

† J. S. Townsend, *ll. cc.*

‡ L. B. Loeb, Phys. Rev. xvii. No. 2, pp. 89–115 (Feb. 1921); Proc. Nat. Acad. Sci. vii. No. 1 (Jan. 1921).

It was presumably nitrogen which had been entrapped in the pores of the marble.

The N_2O used came from a small commercial tank such as is used by the dental profession. It was bubbled through two flasks containing a concentrated fresh solution of $FeSO_4$. From there it passed through two $CaCl_2$ drying tubes and a tube of P_2O_5, through a trap kept at $-70°$ C. to remove the more condensible impurities, and finally into another trap where it was condensed out by frozen alcohol. From this trap the liquid gas was fractionated, the intermediate portion only being admitted to the measuring chamber. The gas finally went through a system of NaOH, $CaCl_2$, and P_2O_5 tubes before passing into the measuring chamber.

In all cases the apparatus was filled by exhausting it to 20 mm. and then running in the gas to atmospheric pressure. When this process had been repeated from four to seven times, depending on what gas had been in the chamber before, the filling was considered complete. The measurements were carried out precisely as described in the earlier work on air. The methods employed by Mr. Wahlin as well as a detailed discussion of his results will be published separately by Mr. Wahlin. The values of n obtained are given in the Table on p. 235.

The results show that this quantity n varies through an enormous range of values. In N_2 and H_2 it is doubtful whether the electron may ever attach permanently to these molecules. In Cl_2, as far as experiments can show, the electron attaches within very few impacts to form chlorine ions. For other gases, n has all values lying between these limits. It is consequently obvious that in spite of the difficulties encountered in determining its value accurately, the constant of electron attachment n *is, even in its order of magnitude, a marked and characteristic property of the different kind of gas molecules.*

In a paper on the "Arrangement of Electrons in Atoms and Molecules," Langmuir * suggests that owing to the fact that the structure of N_2O and CO_2 molecules is quite alike, their properties as influenced by this structure should be the same. This is shown to be wrong as far as the value of n is concerned. The value of n for CO_2 when freshly prepared is $1{\cdot}5 \times 10^7$, while that for N_2O is $6{\cdot}1 \times 10^5$. Furthermore, the value of n for CO_2 undergoes a rapid decrease with time after preparation. This change is not shown for N_2O or for any of the other gases studied. The

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* I. Langmuir, Journ. Am. Chem. Soc. xli. No. 6, p. 898 (June 1919).

TABLE OF RESULTS.

Gas.	*n* from equation (4).	K ionic mobility.	*n* from equation (1).	Limits of variation of *n* on equation (1).	Observer.	Comments.
N_2	Infinite.	2·50	Infinite.	......	Loeb.	Constant with time.
H_2	Infinite.	...	Infinite.	......	Loeb.	Constant with time.
CO	$1{\cdot}6\times10^{8}$	1·20	$3{\cdot}1\times10^{7}$	$(1–6)\times10^{7}$	Wahlin.	Constant with time.
NH_3	$9{\cdot}9\times10^{7}$	0·78	$1{\cdot}3\times10^{7}$	$(0{\cdot}7–1{\cdot}6)\times10^{7}$	Wahlin.	Constant with time.
C_2H_4	$4{\cdot}7\times10^{7}$	0·91	$7{\cdot}1\times10^{6}$	$({\cdot}18–1{\cdot}6)\times10^{7}$	Wahlin.	Constant with time.
C_2H_2	$7{\cdot}8\times10^{6}$	1·15	$1{\cdot}5\times10^{6}$	$(0{\cdot}8–2{\cdot}3)\times10^{6}$	Wahlin.	Constant with time.
C_2H_6	$2{\cdot}5\times10^{6}$	1·30	$5{\cdot}3\times10^{5}$	$(2{\cdot}5–8{\cdot}8)\times10^{5}$	Wahlin.	Constant with time.
CO_2	$1{\cdot}5\times10^{7}$	1·22	$2{\cdot}9\times10^{6}$	$(2{\cdot}3–4{\cdot}3)\times10^{6}$	Loeb.	Freshly prepared.
CO_2	$3{\cdot}5\times10^{6}$	1·22	$6{\cdot}9\times10^{5}$	......	Loeb.	4 hours old.
CO_2	$2{\cdot}1\times10^{5}$	1·22	$4{\cdot}0\times10^{4}$	......	Loeb.	22 hours old.
N_2O	$6{\cdot}1\times10^{5}$	1·33	$1{\cdot}4\times10^{5}$	$(0{\cdot}8–2{\cdot}3)\times10^{5}$	Loeb.	Freshly prepared.
N_2O	$3{\cdot}6\times10^{5}$	1·33	$7{\cdot}8\times10^{4}$	......	Loeb.	24 hours old.
C_2H_5Cl	$3{\cdot}7\times10^{5}$	0·30	$1{\cdot}8\times10^{4}$	$(1{\cdot}3–2{\cdot}8)\times10^{4}$	Wahlin.	Constant with time.
Air	$4{\cdot}3\times10^{4}$	2·50	$1{\cdot}8\times10^{4}$	$(0{\cdot}7–6{\cdot}4)\times10^{4}$	Loeb.	Constant with time.
O_2	$8{\cdot}7\times10^{3}$	2·50	$3{\cdot}6\times10^{3}$	$(1{\cdot}4–5{\cdot}7)\times10^{3}$	Loeb.	Constant with time.
Cl_2	Less than $2{\cdot}1\times10^{3}$	0·73	Less than 240	......	Wahlin.	......

change takes place in the dark, and is similar to an effect found by Wellisch[*] when he studied the mobilities of electrons in CO_2. He found that the mobility rapidly decreased in the gas with an increase of time after preparation. An even more marked effect of this nature was found by Wellisch[†] in the vapour of petroleum ether. The small change in the value of n for N_2O with time was accompanied with an increase in pressure of 13 mm. Such an increase in pressure was possibly due to a decomposition of the N_2O. If this were the case the change in n would be quantitatively accounted for by the oxygen produced in the process.

It has been shown by Mr. Wahlin that the relative energy of impact between electron and molecule does not influence attachment. One may then conclude from the nature of the values of n obtained, that n is dependent on either the electrons striking a particular point in the atom in order to attach, or in its striking a molecule in some particular state of chemical or physical activity.

Summary.

1. The results obtained in a recent study of the mobilities of electrons in pure nitrogen are discussed relative to the theory of the formation of negative ions from electrons and molecules developed by the writer.

2. An equation is arrived at which gives the values of n, the constant of attachment, with a greater degree of certainty than the one previously given. The equation is, however, not yet satisfactory, owing to the lack of knowledge of the electronic mobilities in the various gases.

3. On the basis of the equation derived, the values of n for a number of different gases are given as computed from recent experiments.

4. The results show that in spite of the uncertainties in the determination of n it varies through such an enormous range of values for the different gases, that the order of magnitude of the quantity alone furnishes a characteristic constant of the gas.

In concluding, the writer desires to acknowledge with thanks the assistance of Mr. Wahlin in the preparation and measurements made on the gases CO_2 and N_2O. The writer's thanks are also due to Prof. R. A. Millikan for his kind criticism of this paper.

Ryerson Physical Laboratory,
July 15th, 1921.

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[*] E. M. Wellisch, Am. Journ. Sci. xliv. p. 11 (July 1917).

[†] E. M. Wellisch, *ibid.* p. 15.

XXIV. *Notices respecting New Books.*

Tables of Physical and Chemical Constants. G. W. C. KAYE and T. H. LABY. Fourth Edition. 160 pages. (Longmans, Green & Co., 1921; price 14 shillings.)

THE test of the utility of these Tables is the call for a fourth edition. Alterations and additions have been made relating to the figure of the earth, acceleration of gravity, and the gravitation constant; and the chemical data have been recalculated, using the international atomic weights.

The conventional niggling C.G.S. units are employed throughout. But it will do no harm to point out certain advantages in the M.K.S. system (metre-kilogramme-second), tacitly employed in electrical work units more usual for commercial purposes.

A metre cube (m^3) of water is here the metric tonne (t) of 1000 kg, and density is reckoned in kg/m^3.

The theoretician's objection to the M.K.S. system of making 1000 the density of water is a practical asset, as the last unit figure of the tabulated density of a substance is then affected by the density of the air, to the extent of about 1·25; the density given in the table being absolute density in a vacuum, from which this deduction must be made in a careful weighing carried out in air actually by the human machine, and not merely the mechanical balance alone.

It is curious how this Hospitalier notation should be so long in making its way into use, recommended as far back as 1883 in an International Electrical Congress. No need then for that confusing chapter on Units and Dimensions; these are always kept in view by Hospitalier.

In the M.K.S. units the joule replaces the erg, but no name has been found yet to replace the dyne, equivalent of 100,000 dynes; this force would represent the weight of about 100 g, say 10 pennies, so it cannot be described as large, while the dyne and erg are too microscopic to be used except with high powers of 10 in the index notation.

In matter relating to the figure of the Earth, the circumference should be stated, and the radius or diameter never be mentioned. It is not right in a treatise on Trigonometry for the use of the naval officer to give the radius of the Earth as about 4000 miles, and then not specifying whether it is the military land mile, or the nautical geographical (G) mile that is intended. Only the G mile should be implied, and then the circumference of the Earth is 21,600 miles, as laid down by Roger Bacon in the Opus Majus, and this makes the radius 3438 G miles, a radian arc of 57°·3, or 3438′.

In the Metric System the circumference was made into forty thousand kilometres; and then in these units the slight variations from the true sphere are expressed in a small variation from a large round number.

The mass of the Earth is given, and also of an estimate of the ocean; the mass of the atmosphere may be stated as the mass of an ocean of mercury covering the Earth, of mean depth the average height of the barometer.

The chief value of these tables is in giving the latest measured value of a physical quantity to the number of figures warranted by experiment, and not to wander off into the region of the dishonest decimal.

These accurate statements appear more eloquent and convincing as a small correction on a large round number representing the accepted average value; and risk of error is diminished in the large leading figures of a result in this enormous mass of data.

Stated in logical order, the length l of the seconds' pendulum is the measured quantity, and g is derived from it by the relation $g = \pi^2 l$.

Introduction to the Theory of Fourier's Series and Integrals. By H. S. Carslaw, Professor of Mathematics in the University of Sydney. (Macmillan, 1921, 320 pages; price 30 shillings.)

Although classing itself modestly as a mere Introduction to the subject, the work extends to over 300 pages, and costs 30 shillings; and a sequel seems promised in the future to a complete treatise.

This is very complete at present in a rigorous examination of the nature of the convergency and continuity of the Fourier series, a succession of fluctuating harmonic terms, equivalent of the harmonics of the monochord, with frequency in the ratio of the integer 1, 2, 3, ... , or wave-length in the harmonic progression of the reciprocal.

These are the commensurable periods in the terms of a Fourier series. But in the Lunar and Planetary theory the various anomalies are resolved into terms of different incommensurable period, such as evection and variation.

The Fourier series is a summation of the harmonics of commensurable period such as those produced on the monochord, and the theory was born of the representation of any arbitrary musical vibration of the chord by a resolution into the pure harmonics.

The legitimacy was disputed by the originators of the idea, d'Alembert, Euler, Bernoulli; but Lagrange settled the question on the modern point of view, although the difficulties and objections raised by Euler still exist, and form the bulk of the discussion in this treatise.

The new mathematician is interested chiefly in what may be called the morbid pathology of the series, in its behaviour at points of discontinuity where a differentiation may be expected to break down, and the convergence requires examination, whether regular, uniform, or not.

But the man who employs the series in an application to an electrical alternating current, or to the balance of quick running machinery, will look at the question in a reverse order. This is the outlook contemplated by Professor Perry. He takes a few well chosen harmonic terms at the beginning of a Fourier series, and examines the shape of the resulting graph, to see if it is a good imitation of the mechanical result under examination; in a problem such as machinery balance or electrical surging.

To raise the peak of a curve and to sharpen it if too blunt, an odd harmonic would be introduced; the effect of the even harmonic is felt in enlarging the haunches of a wave-arch.

The figures in Chap. VII will give a lead in this treatment, how to smooth out ripples if too prominent.

Starting with an arbitrary Fourier series, such as on page 3, and denoting it by

$$\tfrac{1}{2}a_0 + \ldots. + a_p \cos p\pi x/l + b_p \sin p\pi x/l + \ldots. = f(x) = y,$$

then, in the interval $l > x > -l$, the coefficient a_p is the average $y \cos p\pi x/l$, and b_p is the average $y \sin p\pi x/l$; and so Fourier's theorem is stated without using the language of the Integral Calculus, in a form that appeals to a practical mathematician; and the operation of averaging can be carried out mechanically by wrapping the curve of y round a cylinder, once, twice, thrice, ...

Simple statement of this kind is required in an appeal to the interest of the beginner.

In the applications, the a and b coefficients appear usually as rational numbers, as for instance in the representation of $y=1-x$. But the Jacobian zeta function, zn xK, is penultimate to this curve, as $\kappa \longrightarrow 1$; the curve, a straight line, is imitated without any ripples or discontinuities, and the Gibbs phenomenon of p. 268 is absent.

So too the curves of sn xK or cn xK may be investigated in the penultimate form of $\kappa \longrightarrow 1$, in their representation of broken straight lines. Here the a and b coefficients are transcendental numbers.

This is the method of the average, described and resumed in § 95, but a further discussion is inaugurated, as the statement of the average is considered quite incomplete and inconclusive by the author; and Dirichlet's conditions of § 91 are to be satisfied in the interval, leading to very delicate and abstruse consideration, in which the author spreads himself to his own delight.

He will not allow a proper comprehension of Fourier's Series and Integral without a knowledge of what is involved in the convergence of infinite series, and integrals; and the Definite Integral is treated in Chapter IV from Riemann's point of view.

The volume is called an Introduction because the original work is to be divided into two parts, the second part devoted to a mathematical discussion of Heat Conduction, where the most interesting applications are to be found, sequel to Fourier's *Théorie de la Chaleur*, of 1822.

The Mechanical Principles of the Aeroplane. By S. Brodetsky, Reader in Applied Mathematics, University of Leeds. (J. & A. Churchill, 1921, 270 pages; price 21 shillings.)

This treatise goes very deeply and thoroughly into the mechanical and mathematical calculations involved in the design of the flying machine.

An introduction discusses the possibility of flight of a machine heavier than air, and might well be amplified to show the main facts involved, after the resistance was taken to vary as the simple sine law instead of the squared sine, as required on Newton's method of treating air as a cloud of dust particles, ignoring the equation of continuity.

But as soon as the theoretical work of Helmholtz and Kirchhoff on discontinuous flow of a fluid pointed out the simple sine law as much more appropriate, it was seen that mechanical flight was in the region of possibility, and had only to await the arrival of an engine of weight per horse-power low enough. This was provided happily by the advent of the motor vehicle and its internal combustion engine as a present ready made, and then man could really take to the air, and not merely dream of it in the realm of poetical fancy.

Such an introduction need not go beyond calculations to appeal to the young scholar, and would serve to attract him further into the deeper treatment given here, as in other complete treatises, such as Bairstow's 'Applied Aerodynamics.'

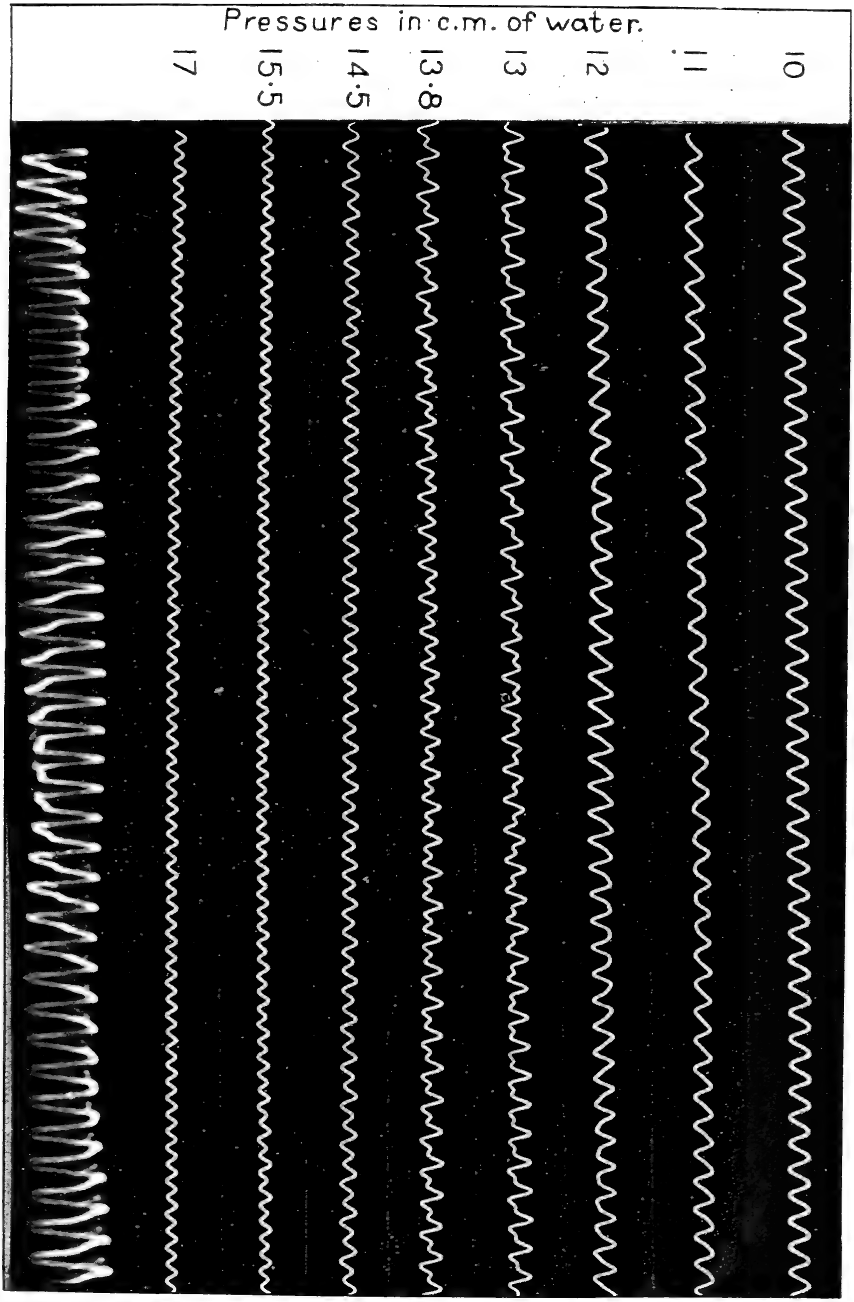
Optical Theories. By D. N. Mallik, Professor, Presidency College, Calcutta. Second Edition revised. 200 pages; 16 shillings. (Cambridge, at the University Press, 1921.)

A course of lectures delivered before the Calcutta University to advanced students on Optical Theories.

Early speculations, on the corpuscular and the undulatory theory, are discussed in Chap. I. The elastic solid theory, electro-magnetic theory, and electron theory follow in Chaps. II, III, IV. In this new edition a discussion is introduced in Chap. V of the new theory of Relativity, in its bearing on the modification of former theories of the æther.

These various theories are summarised and compared, in a valuable discussion in eloquent words in Chap. VI, of the nature of the electro-magnetic field.

In this way the true inner significance is brought to light of the accurate interpretation of the results concealed in the differential equations and triple integrals of the rigorous mathematical treatment.


Pressures in c.m. of water.
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THE
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FEBRUARY 1922.

XXV. *On the Application of Probabilities to the Movement of Gas-Molecules.* *By* Prof. F. Y. Edgeworth, *F.B.A.**

THIS is a sequel to the paper bearing the same title in the Philosophical Magazine for September 1920. The three arguments there employed to determine the distribution of velocities in a molecular medley are here reinforced.

I. Laplace's Theory of Error.

The first argument was based on the leading property of the law of error first stated by Laplace. The enunciation was facilitated by the fiction of molecular movement in one dimension. Two sets of perfectly elastic piston-shaped particles were supposed to be moving in one and the same right line under stated conditions (*loc. cit.* p. 249).

1. *The form of the frequency-function.*—It was shown that, whatever the initial distribution of the velocities U and u pertaining to particles of mass M and m respectively, the system would through repeated collisions be ultimately distributed according to the normal error function

$$(\mathrm{N}\sqrt{\mathrm{A}a/\pi})\ \exp -(\mathrm{AU}^2+au^2). \quad . \quad . \quad . \quad (1)$$

That is, presuming that the two sets of velocities fluctuate *independently*. Otherwise the ultimate distribution can be written

$$(\mathrm{N}\sqrt{\mathrm{A}a}/\pi\ \sqrt{1-r^2})\ \exp -(\mathrm{AU}^2-2r\ \sqrt{\mathrm{A}a}+au^2)/(1-r^2). \ (2)$$

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* Communicated by the Author.

This may mean that, if we select all the members of one class (in a unit of the medley), say those between U and $U+\Delta U$, and observe the velocities of those molecules belonging to a different set which are nearest to a member of the selected class, the distribution of the array thus presented will not be that of the u-velocities in general, but one more closely congregated about a centre, rU.

The essential condition for this consummation is the *linear relation* between the velocities U and u of two particles about to collide and the resulting velocities U' and u':

$$\left.\begin{aligned} U' &= (M-m)U+2mu \\ u' &= 2MU+(m-M)u \end{aligned}\right\}; \quad . \quad . \quad . \quad . \quad (3)$$

if $M+m=1$ (*loc. cit.* pp. 250, 251).

When we go on to two dimensions, considering first perfectly elastic circular disks moving over a perfectly smooth plane, the essential condition still persists. But the coefficients of the linear function are not now as in the simplest case (3) the same for every collision. They involve a variable parameter, the sine or cosine of an angle θ, made by the line of centres at the moment of collision with the direction of the relative velocity (or with a fixed axis) (*l. c.* p. 259). But the presence in the coefficients of such a parameter hovering in random fashion about an average is not fatal to the genesis of the law of error. This was pointed out in the original paper (p. 262) with reference to a later stage, the impact between molecules with several degrees of freedom. The principle should have been introduced at an earlier stage; and it might have been employed at a still later stage, namely with reference to *encounters* as distinguished from collisions.

Consider molecules with several degrees of freedom such as chains—bars linked by hinges—moving over a perfectly smooth plane. Let the generalized components of momentum P_1, $P_2 \ldots P_5$; p_1, $p_2 \ldots p_5$ be changed by an impact to P_1', $P_2' \ldots$; p_1', $p_2' \ldots$. Each of the latter set may be regarded as a linear function of the original components; the coefficients now depending not only (as in the simple case of disks) on the relative position of the mass-centres (before the encounter), but also on the co-ordinates. Still the coefficients of the linear functions connecting the P''s with the P's may be regarded as hovering about a mean value; and accordingly the law of error will be set up. This reasoning reinforces the proof which was before offered in the case of encounters (*l. c.* p. 268); based on the mean powers of a magnitude which is a *function other than linear* of numerous independently fluctuating elements.

These conclusions and those which follow are readily extended from two to three dimensions.

2. *The constants of the frequency-function.*—The form of the sought function having been ascertained, we have next to evaluate the constants. For this purpose we might obtain aid from one of the other arguments, from the third as before (*l. c.* pp. 252, 263), or from the second (below II. 1) if employed to determine the *constants*, the *function* being given. Otherwise, supposing the ultimate stable distribution of velocities to have been reached, observe the velocities in any assigned direction, *e. g.* U, for numerous specimens presented at random by molecules of the type M. Their average velocity in that direction ought to be the same as the average of any other large set of U-velocities, in particular the set which is formed by molecules of the selected class meeting with molecules of the *m* type. This condition requires certain relations between the coefficients of the frequency-function. In the simplest case where the function is of the form (1) the U of any M particle colliding with any *m* particle becomes by (3) U′, where

$$U' = (M-m)U + 2mu.$$

Since $[U'^2] = [U^2]$, square brackets denoting mean value, we have

$$[U^2]^2 = (M-m)^2[U^2] + 4m^2[u^2]; \quad . \quad . \quad . \quad (4)$$

the mean value $[Uu]$ being zero (if the mass-centre of the system is zero). Now from (1) we have

$$[U^2] = 1/2A, \text{ and } [u^2] = 1/2a.$$

Substituting in (4) and multiplying by 2A, we have

$$1 = (M-m)^2 + 4m^2A/a \text{ (if } M+m=1).$$

Whence $a/m = A/M$. Thus the index of (1) is of the form

$$-\lambda(MU^2 + mu^2). \quad . \quad . \quad . \quad . \quad . \quad (5)$$

If the frequency-function is of the form (2) substitute $1/A(1-r^2)$ and $1/a(1-r^2)$ for $1/A$ and $1/a$ in the preceding argument; and a similar conclusion will be reached. The index will now be of the form

$$-\lambda(MU^2 - 2r\sqrt{Mm}Uu + mu^2)/(1-r^2). \quad . \quad . \quad (6)$$

For the general case of molecules with several degrees of freedom we may use the formulæ for the components of momentum after impact between such molecules (*l. c.* p. 261).

Transform the system by a linear (preferably orthogonal) substitution so that T the kinetic energy assumes the form

$$B_1\Pi_1{}^2+B_2\Pi_2{}^2+\ldots+b_1\pi_1{}^2+b_2\pi_2{}^2+\ldots; \quad . \quad . \quad (7)$$

where the B's and b's are functions of the co-ordinates, the Π's and π's are "momentoids." The general expression for $\Pi_1{}'$, what Π_1 becomes in consequence of a collision, in terms of the Π's, viz. $\Pi_1-\Lambda_1R$, then reduces to

$$\Pi_1{}'=\Pi_1-2\Lambda_1\frac{(\Lambda_1B_1\Pi_1+\Lambda_2B_2\Pi_2+\ldots-\lambda_1b_1\pi_1-\lambda_2b_2\pi_2-\ldots}{\Lambda_1{}^2B_1+\Lambda_2{}^2B_2+\ldots+\lambda_1{}^2b_1+\lambda_2{}^2b_2+\ldots};$$

where Λ_1, $\Lambda_2\ldots\lambda_1$, $\lambda_2\ldots$ correspond to the L_1, $L_2\ldots l_1$, $l_2\ldots$ etc. as defined in the general case (*l. c.* p. 262); and B_1, $B_2\ldots b_1\ldots$ correspond to B_{11}, $B_{22}\ldots b_{11}\ldots$; except that the momentoids are not (in general) true (Lagrangian) components of momentum (a circumstance which does not affect the present argument concerned only with collisions and the attendant impulses). Forming the mean square for components of momentum (the mean obtained by supposing the velocities to acquire all possible values while the co-ordinates and points of impact remain the same), and equating $[\Pi_1{}'^2]$ to $[\Pi_1{}^2]$, and remembering that the mean products $[\Pi_r\,\Pi_s]$ vanish, we obtain

$$\left.\begin{array}{l}-4\Lambda_1{}^2\Lambda_2{}^2(B_1B_2[\Pi_1{}^2]-B_2{}^2[\Pi_2{}^2]\\ -4\Lambda_1{}^2\Lambda_3{}^2(B_1B_3[\Pi_1{}^2]-B_3{}^2[\Pi_3{}^2]\\ .\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\\ -4\Lambda_1{}^2\lambda_1{}^2(B_1b_1[\Pi_1{}^2]-b_1{}^2[\pi_1{}^2]\\ -4\Lambda_2{}^2\lambda_2{}^2(B_1b_2[\Pi_1{}^2]-b_2{}^2[\pi_2{}^2]\\ .\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\end{array}\right\}=0.$$

Now it is known (by I. 1) that the sought frequency-curve is of the form

$$\text{Const. exp}-(C_1\Pi_1{}^2+C_2\Pi_2{}^2+\ldots+c_1\pi_1{}^2+c_2\pi_2{}^2+\ldots).$$

Put $\qquad C_1=K_1B_1,\ C_2=K_2B_2,\ \ldots c_1=k_1b_1;$

and the last written equation becomes

$$-2\Lambda_1{}^2\Lambda_2{}^2(B_1/K_1-B_2/K_2)-2\Lambda_1{}^2\Lambda_3{}^2(B_1/K_1-B_3/K_3)\ldots$$
$$-2\Lambda_1{}^2\lambda_1{}^2(B_1/K_1-b_1/k_1)-\ldots=0.$$

Since this equality holds good for all the values which the Λ's and λ's can assume as the points of contact vary (the *co-ordinates* remaining the same), it follows that

$$K_1=K_2=K_3\ldots=k_1=k_2.$$

Thus the frequency-function is of the form (8) Const. exp $-\lambda T$; where T is the kinetic energy (7), and λ is determined by the condition that the energy of the system for any assigned values of the co-ordinates is constant (*l. c.* p. 263).

This reasoning may at once be extended to *encounters* in the case of motion in one dimension since the relevant equations (3) are in that case the same for collisions and encounters. In the case of disks on a plane the conservation of energy and that of momentum give only three equations for the four resultant velocities U', V', u', v'. A fourth condition is presented by assigning the angle 2θ through which the direction of the relative velocity is turned by a collision or encounter. There can therefore be always arranged a fictitious collision which has the same effect in changing the velocities as any given encounter. Replacing each encounter by the equivalent collision, we can transfer to encounters the conclusion which has just been proved for collisions. An equivalent collision is not so simply obtained when there are several degrees of freedom. Let us pass to this case by supposing one set of disks to have its centre of mass different from the centre of shape. The angle between the line joining those points and a fixed axis, say ϕ, defines the phase of an encounter. We may now conceive a second disk of the other (symmetrical) type to be in contact with the first at any point on the periphery thereof. But we thus obtain only four equations to determine the five quantities U', u', V', v' and $\dot{\phi}'$ the changed velocity of rotation. To obtain another equation let us artificially create a second point of impact by affixing a sort of buffer or tentacle (of negligible mass) to the first disk and arranging that there shall be simultaneous impacts at two points. Generalizing the formulæ given for impact at one point (*l. c.* p. 262), we shall now obtain Π_1', $\Pi_2' \ldots \pi_1'$ in terms of Π_1, $\Pi_2 \ldots \pi_1 \ldots$ and two sets of the coefficients called Λ, λ, each set depending on the position of a point of contact. We have thus with the three conditions given by the conservation of energy and that of momentum two additional variables, whereby to secure an impact equivalent to the encounter. It would not, however, be an exact equivalent. For the angle ϕ would in general be changed by an encounter, but not by the impact. But since the values of ϕ occur with uniform distribution, the frequency-distribution of the actual system would be the same as that of the artificial system. The reasoning may be extended to the general case where there are several "momentoids."

3. *Correction of the normal formula.*—There is reason to believe that the conditions for the genesis of the normal law are not perfectly fulfilled by a molecular chaos. With regard to collisions, the elasticity can hardly be regarded as perfect (Cp. Burbury, Science Progress, vol. ii. § 7). In the case of encounters, the beginning and the end of the encounter being defined arbitrarily, it is to be apprehended that there may be some slight interaction between the molecules. Both in the case of collisions and encounters the ultimate velocities have elements in common (*l. c.* p. 251). If the independence of the elements aggregated and the linearity of the aggregation is not perfect, the function proper to represent the frequency of the aggregate would no longer be the simple normal law, but the corrected form described by the present writer as the *generalized law of error* (Cambridge Philosophical Transactions, 1904 ; Journal of the Royal Statistical Society, 1906). The first correction, involving odd powers of the variables, may presumably be neglected. The formula given by second correction may be written in the simple case of motion in one dimension

$$\begin{aligned}\mathrm{F}\times\{1+\alpha(\tfrac{1}{2}-2\mathrm{MU}^2+\tfrac{2}{3}\mathrm{M}^2\mathrm{U}^4)+\beta(\tfrac{1}{2}-2mu^2+\tfrac{2}{3}m^2u^4)\\ +\gamma(1-2\mathrm{MU}^2)(1-2mu^2)\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)\end{aligned}$$

where F is the normal function (1), α, β, γ are small coefficients proportional to the excess of the respective mean powers $[\mathrm{U}^4]$ $[u^4]$ $[\mathrm{U}^2u^2]$ over what each would be if the normal law were perfectly satisfied (Camb. Phil. Trans. *loc. cit.* p. 118, 1904).

The above expression, which may be written as a function of U multiplied by a function of u, if $\gamma=0$ ($\alpha\beta$ being negligible), need not express correlation between the velocities. What slight interdependence there may have been among the *elements*—the long series of velocities from which the U and u in (1) resulted—may have disappeared in the compound (Camb. Phil. Trans. p. 126, 1904).

4. *Correlation.*—The correction above made may, however, co-exist with (normal) correlation. Our first argument is not inconsistent with Dr. Burbury's contention that there may be some interdependence between the velocities of contiguous molecules (Science Progress, vol. ii. § 33, 1894 ; Phil. Trans. 1886 : 'Dense Gases,' § 13 ; 'Kinetic Theory of Gases,' p. 11 ; *et passim*). But there are two cases of interdependence which should be excluded from the field to which (2) applies, namely (*a*) between molecules in an *initial* distribution, or *on their way* to the ultimate normal

distribution; (*b*) between molecules engaged in an encounter (referred to below, III. 3).

5. *Controverted points.*—Our first argument has a bearing on some vexed questions. Thus with respect to "time-averages" it would hardly occur to one impressed with Laplace's theory of error to question Lord Rayleigh's statement that "for a single particle the time-averages of (u^2 and U^2) are equal, provided the averages be taken over a sufficient length of time" (Phil. Mag. ser. 5, vol. xlix. (1900) p. 108). Again as to the reversibility of the motion, consider Galton's mechanical illustration of the law of error. Shot is poured in through an aperture at the top of the apparatus and comes out at the bottom after repeated collisions with interposed obstacles in the form of the normal curve ('Heredity and Genius,' p. 63; Yule, 'Theory of Statistics,' p. 298). Need we trouble ourselves with the thought that if the shots were dropped into the apparatus in numbers corresponding at each point to the normal distribution (say by turning the mechanism upside down) they *might* come out, after repassing the obstacles, in exactly the same arrangement as that in which they first entered. Recognition of the leading law of Probability disposes the disciple of Laplace to accept the warning of De Morgan, repeated by Tait with reference to the Kinetic Theory of Gases (Transactions Roy. Soc. Edinburgh, vol. xxxiii. p. 256): "No *primary* considerations connected with the subject of *probability* can or ought to be received if they depend upon the results of a complicated mathematical analysis."

II. THE "H" THEOREM.

The second argument is based on the use of "H," defined as the integral between extreme limits of $f \log f$, where f is the sought frequency-function of the velocities (or the same multiplied by, or with the addition of, a constant, *l. c.* p. 253). The argument is to be distinguished from those in which "H" is employed together with the premiss that the frequency-distributions of the colliding molecules are *independent*, *e. g.* by Boltzmann ('Gastheorie,' I. 5) and by Jeans in his *first* appeal to the "H" theorem ('Dynamical Theory of Gases,' 3rd ed., Art. 15 *et seq.*). Without that assumption it is argued that the sought function f is that which makes "H" a minimum subject to the constancy of the energy (and momenta) of the system.

1. *Character of the argument.*—The method is akin to the use of Probabilities for the determination of *constants* pertaining to functions of a given form when the data consist

of *percentiles* (*l. c.* p. 254 and references there given). Both problems involve the following fundamental principle. Suppose a sample numbering N is extracted at random from an indefinitely large medley of things, divided into classes such as (sets of) balls numbered 1, 2, ... m and mixed in proportions $\nu_1 : \nu_2 \ldots \nu_{m-1} : \nu_m$, where $\Sigma\nu = \mathrm{N}$.

Let $\mathrm{F}(n_1, n_2 \ldots n_m; \nu_1, \nu_2 \ldots \nu_m)$ be the probability that from a given set of ν's there will result a specified set of n's (and accordingly $\mathrm{F}(\nu_1, \nu_2 \ldots \nu_m; n_1, n_2 \ldots n_m)$—the variables and constants changing places—the probability that a given set of n's will have resulted from a specified set of ν's). Then if the extraction is subjected to a condition which the n's must satisfy (sets not satisfying that condition being rejected), the most probable set of n's, corresponding to a given set of ν's, is found by making $\mathrm{F}(n_1, n_2, \ldots; \nu_1, \nu_2 \ldots)$ a maximum *subject to* the imposed conditions (with a like proposition relating to ν's inferred from n's). For instance let $\mathrm{N}=30$; and $\nu_1=\nu_2=\nu_3=10$. And let there be imposed on the n's the condition $n_2=2n_1$. We have then to maximize the expression

$$(1/3)^{30}\, 30\,!/n_1\,!\; n_2\,!\; n_3\,! + \lambda(n_2 - 2n_1) + \mu(n_1 + n_2 + n_3 - \mathrm{N}),$$

where λ and μ are indeterminate multipliers. The required set is found with the use of a Table to be $n_1=7, n_2=14, n_3=9$.

Let $n_1, n_2 \ldots$ be all large. Then by Stirling's theorem, $\log \mathrm{F}(n_1, n_2 \ldots \nu_1, \nu_2 \ldots)$ becomes approximately

$$\text{Const.} - n_1 \log n_1 - n_2 \log n_2 \ldots + n_1 \log \nu_1 + n_2 \log \nu_2 + \ldots \quad (10)$$

The variable part of this expression may be called H as being *in eodem genere* with the "H" above defined. (In the inverse problem of percentiles where the ν's are to be determined subject to the condition that they are given functions of certain sought quantities, it is presumed that the differences $(\nu - n)$ are small; whereby Taylor's principle becomes available, and H reduces to the Pearsonian χ^2; *l. c.* p. 254.)

Let the given ν's be all equal, the latter terms of (10), $n_1 \log \nu_1 + n_2 \log \nu_2 \ldots$, thus becoming absorbed in the constant part (since $\Sigma n = \mathrm{N}$). Let the n's be represented by columns standing on equal bases, numbered 1, 2, 3 ... r, $r+1$, .. on the right of a central point, and -1, -2, -3 ... $-r$, $-(r+1)$ ... on the left. Let there be imposed the condition

$$\Sigma \mathrm{M} r^2 (n_r + n_{-r}) = \mathrm{R}^2$$

(R a given large number); the summation extending over all possible values of n. We have thus to minimize

$$\Sigma n_r \log n_r + \Sigma n_{-r} \log n_{-r}$$
$$+ \lambda(\Sigma \mathrm{M} r^2 (n_r + n_{-r}) - \mathrm{R}^2) + \mu(\Sigma(n_r + n_{-r}) - \mathrm{N}).$$

Whence $\log n_r = \log n_{-r} = \text{Const.} - \lambda M r^2$.

Put $U = r\Delta U$; $\lambda = A(\Delta U)^2$; $R^2(\Delta U)^2 = N2E$,

and there results for the distribution of U,

$$\Delta U \text{ Const. exp } -AMU^2 \text{ ; } \quad . \quad . \quad . \quad . \quad (12)$$

where A is to be determined by treating ΔU as a differential, multiplying (12) by U^2 and integrating with respect to U between $+\infty$ and $-\infty$, and equating the result to N2E (the outside constant securing that $\Sigma n = N$). By parity if U and u are selected by a random sortition from an indefinite number of values demarcated respectively by the small finite differences ΔU and Δu, subject to the condition

$$\Sigma\Sigma(MU^2 + mu^2)\Delta U\,\Delta u = \text{constant},$$

the most probable distribution of U and u—the one which in a prolonged series of trials will be most frequently attained, and around which the sets of N will hover—is

$$\Delta U \Delta u \text{ Const. exp } -\lambda(MU^2 + mu^2). \quad . \quad . \quad (11)$$

When differentials are substituted for finite differences this may be described as the function which minimizes "H," subject to the imposed condition (expressed as an integral).

2. *Legitimacy of the argument.*—May we regard the velocities in a molecular medley as analogously determined by a sortition subject to the conditions imposed by Dynamics? The high authority of Professor Jeans may be appealed to in favour of this view ('Dynamical Theory of Gases,' 3rd ed. § 54 *et passim*). He confirms too the connected proposition that the distribution of velocities in the medley tends to and hovers about some ultimate form. Tait has thus expressed the presumption in favour of this proposition : "Everyone who considers the subject .... must come to the conclusion that continual collisions among our set of elastic spheres will .... produce a state of things in which the percentage of the whole which have at any moment any distinctive property must (after *many* collisions) tend towards a definite numerical value; from which it will never afterwards markedly depart"—with certain reservations (Trans. Roy. Soc. Edinb. vol. xxxiii. p. 67). Professor Jeans confirms this presumption when he shows, with the aid of Liouville's theorem, that certain incidents adverse to the presumption are not to be apprehended (Encyclopædia Britannica, ed. 11, Art. *Molecule*, p. 658 ; Phil. Mag. ser. 6, vol. vi. (1903) p. 722).

3. *Analogy of the law-of-error in general statistics.*—The legitimacy of the argument is confirmed by its use outside molecular dynamics to prove that the normal error-function is the ultimate form approached by the continued superposition of independently fluctuating statistics; subject to the condition that the mean square of the compound is constant (*l. c.* p. 256; and cp. p. 269). The analogy throws light on the implicated question whether there be an ultimate form and its connexion with Liouville's theorem. The existence of such a form is presumable on grounds of common sense. But hesitation may be felt when we deal with an unfamiliar case. Suppose MU to be the amount of money possessed by a person of one class, and mu by one of another class; and that on a deal between them U becomes U′ and u, u', in virtue of the conditions

$$\mathrm{MU}^4+mu^4=\mathrm{MU}'^4+mu'^4 \text{ and } \mathrm{MU}+mu=\mathrm{MU}'+mu'$$
$$(\mathrm{M} \text{ and } m \text{ constants}).$$

Let there occur an immense number of such transactions; while the sum-total of $\mathrm{MU}+mu$, and likewise of MU^4+mu^4, in the society remains constant. May we apply the second argument and conclude that the money will be ultimately distributed among the individuals according to a law of frequency of which the logarithm is

$$\text{Constant } -\lambda(\mathrm{MU}^4+mu^4)+\mu(\mathrm{MU}+mu)\ ?$$

The answer is supplied by Liouville's theorem. If a stable state is attained, the frequency-distribution for U and u must be the same as for U′ and u', the values into which U and u pass by a transaction of the kind supposed. Now the frequency-distribution of U′ and u' (given functions of U and u) is obtainable from that of U and u, viz. (hypothetically)

$$\Delta\mathrm{U}\,\Delta u \text{ Const. } \exp\ -\lambda(\mathrm{MU}^4+mu^4)+\mu(\mathrm{MU}+mu),$$

by substituting in the *integral* part of the above expression for U and u their values in terms of U′ and u', and for the differential factor

$$\Delta\mathrm{U}\,\Delta u, \quad \Delta\mathrm{U}'\Delta u'\left(\frac{d\mathrm{U}}{d\mathrm{U}'}\frac{du}{du'}-\frac{d\mathrm{U}}{du'}\frac{du}{d\mathrm{U}'}\right). \quad . \quad (13)$$

The first substitution leaves the integral value unaltered. Accordingly it is necessary to stability that the bracketed factor of $\Delta\mathrm{U}'\Delta u'$ in (13) should be identically equal to unity: that is, that the theorem proved by Liouville and his followers for a conservative dynamical system should hold good.

To apply this criterion to the proposed problem; let us first try to find linear functions for U and u in terms of U' and u', say $U=AU'+Bu'$ and $u=aU'+bu'$. The Liouville condition gives one equation for the coefficients, viz. $Ab-aB=1$. Two more equations are given by the identity $MU+mu\equiv MU'+mu'$; and *five* more by the identity $MU^4+mu^4\equiv MU'^4+mu'^4$. Though these eight equations are not all independent, it will not be possible to find values of the variables which satisfy them all; even admitting imaginary roots. If the value of U, and likewise u, in terms of U' and u' is other than linear, it appears necessary to increase the number of equations, with the result that a solution is unattainable.

It is therefore significant that when the conditions imposed are the conservation of energy and of momentum, the condition (13) is fulfilled by the expressions for U and u in terms of U' and u' in the simple case of one dimension (1); and likewise in more complicated collisions and encounters.

4. *Dense gases.*—The analogy of general statistics suggests a warning against the danger of supposing that the premiss of *independence* (above II. 1) ignored by the second argument is otiose. Consider a normal surface formed by the superposition of n two-dimensioned elements with laws of frequency

$$\zeta_1=\phi_1(\xi_1,\eta_1),\quad \zeta_2=\phi_2(\xi_2,\eta_2)\ldots \quad . \quad . \quad . \qquad (14)$$

Let $({}_1\xi_r, {}_1\eta_r)$, $({}_2\xi_r, {}_2\eta_r)\ldots$ be successive concurrent values of the variables pertaining to ϕ_r; and let

$${}_sx={}_s\xi_1+{}_s\xi_2+\ldots+{}_s\xi_n,\quad {}_sy={}_s\eta_1+{}_s\eta_2+\ldots+{}_s\eta_n\,;$$

the ξ's and the η's and accordingly the aggregate x's and y's being measured from their respective average values (Camb. Phil. Trans. p. 116, 1904). Given that the mean value of Mx^2+my^2 is constant, we might conclude by the second argument that the frequency-distribution of x and y was of the form Const. $\exp -\lambda(Mx^2+my^2)$. But if the values of ξ and η in each element are not independent, the distribution of the x's and y's will not be of that form, but of one like (2) above, containing the *product* of the variables in the index. Yet the argument is not fallacious; it gives the right answer *relating to the data*, which is all that can be expected from Probabilities (Cp. Keynes, 'Probability,' ch. 1, *et passim*). The answer would be true on average in the long run of different instances if positive and negative correlation were equally probable (a supposition perhaps not relevant here). It is true of any particular case on the supposition that we no longer tabulate each y against the x with which that y is formed concurrently, but having dispersed the y's take an x and *any* y at random. These considerations may assist in interpreting the proposition that "the law of distribution of velocities .... remains the same right up to the extreme limiting case in which the spheres are packed so tightly in the containing vessel that they cannot move" (Jeans, 'Dynamical Theory of Gases,' § 57, 3rd ed.). The law of distribution does not hold true of contiguous molecules in the same sense as when the independence of the velocities is postulated. The proposition may be equally true, but it is not equally informing as that which is based on the postulate of independence.

III. On the Lines of Maxwell.

The third argument is based on the incidents of collisions and encounters without the aid of "H." It is now attempted to prove by this argument that the normal distribution is necessary (as well as sufficient; *l. c.* p. 256). The attempt is discouraged by high authorities (Boltzmann, 'Gastheorie,' i. § 5; Watson, 'Kinetic Theory of Gases,' § 14); but it is countenanced by Maxwell when he argues that the normal distribution of velocities is not only "a possible form," but "the only form" ("Dynamical Theory of Gases," 'Scientific Papers,' vol. ii. p. 45). The proof which he gives in that context is indeed very different from that offered here; which is, rather, akin to the reasoning in Maxwell's paper "On the final state of a system of molecules" (*loc. cit.* p. 351).

1. *Proof that the normal distribution is necessary to stability.*—Let us begin with the simple case of disks moving in a plane (as above, I. 1): two sets of disks of mass M and m respectively, and radius at first supposed the same for both sets, say R. Let N be the number of disks of each type in a unit of area; the unit being taken so that N is large. The total area occupied by disks is $2N\pi R^2$. Call the ratio of this to the unit of area ρ, supposed a small fraction, say 1/1000 or less. On a view of the medley at any instant the number of disks which may be expected in an assigned area A is $\rho A\pi/4$. If a small area, say a multiple much less than a thousand of R^2, includes a disk of one set, the frequency with which (at the moment of inspection within a unit area) it will include a disk of the other set is of the order $N\rho$. Likewise the probability that a disk taken at random should have in close proximity two disks (of assigned sets) is of the order $N\rho^2$. These propositions are

easily extended to the case of radii and numbers which are not the same, only of the same order of magnitude.

Each set of disks is divided into *classes* defined by rates of velocity. Thus one class consists of disks with velocities respectively between U and $U+\Delta U$, V and $V+\Delta V$. The distribution of these velocities is represented by the frequency-function $F(U, V)$; meaning that in a unit area the number of disks of the class specified is $NF(U, V)\Delta U\Delta V$. The function $f(u, v)$ is similarly related to the other set. It is required to determine the functions F and f so that the distribution of velocities may be stable.

Observing the unit area, note all the couples of disks which are in such close proximity that within the short time τ (measured forward or backward from the present instant) they either will come into collision, or have come into collision. The species of couples so defined presents two sections according as the partners are consilient or dissilient, say positive and negative sections.

Now let each species of couple be divided into *varieties* (*l. c.* p. 260) defined by the mutual orientation of the disks which are just coming into, or from, collision. Say a variety consists of those couples for which the point of impact on one of the pair is between s and $s+\Delta s$, s being the length of an arc measured from a fixed point (rotation being ignored). The *content* (the number of instances in a unit area) of each variety thus defined will not be the same; but whatever it is it may be assumed to remain constant; on the hypothesis of a random distribution irrespective of position in space. Let us designate the positive (consilient) section of a variety $(U, V;\ u, v)s$ and the corresponding negative $(u, v;\ U, V)s$. Let U', V' and u', v' be the velocities which result from the collision corresponding to the positive section of the specified variety. Then the new velocities will belong to the section $(u', v';\ U', V')s$: the negative section of a variety which may be termed the *reciprocal* of the former.

Observing the medley during the short time τ, we may expect that the whole initial content of the positive section $(U, V;\ u, v)s$ will have passed into the negative section of the reciprocal variety. *Less* than the whole content could not have passed out of the specified section unless one of the disks included therein were before collision with its partner knocked away by a third disk. But this could only happen through the very improbable double event of a third disk being initially in the neighbourhood and also in such a position and with such velocities as to hit one of the partners within the time τ. *More* than the whole initial content could not have passed from the section $(U, V ; u, v)s$, unless during τ a new positive couple of that variety had been created. But this could only happen through a very improbable event; not only must there be initially (within the unit area) a disk belonging to the same class as one of the specified variety—say of mass M with velocities U, V—with *two* disks in the neighbourhood, one of them of the m type, but also the position and velocities of those second and third disks must be such that they shall collide with each other during the time τ and one of them of the m type should acquire the velocities u, v and the orientation with respect to the first disk which the specified variety connotes. By parity of reasoning the whole initial content of the reciprocal section $(u, v ; U, V)s$ will have passed out of that section during the time τ; and the final content of the reciprocal section will consist of the disks comprised initially in the section $(U, V ; u, v)s$. But on the hypothesis of stability the final content of the reciprocal is equal to its initial content. Thus initially and constantly the content of $(U, V ; u, v)s$ is equal to that of $(u', v' ; U', V')s$. Let the relative velocity of the partners in a positive section be w; and accordingly in the reciprocal negative, $-w$. Let the breadth of a section be $\alpha = \Delta s \cos\theta$, where θ is the angle made by the line of relative velocity with the line joining the centres at the moment of impact. Then, if at first the distributions F and f are supposed independent, we have, equating the content of the section to that of its reciprocal,

$$w\tau\alpha\,\Delta U\,\Delta V\,\Delta u\,\Delta v\,F(U, V)\,f(u, v)$$
$$= w\tau\alpha\,\Delta U'\,\Delta V'\,\Delta u'\,\Delta v'\,F(U', V')\,f(u', v').$$

The differential factors, the product of small finite differences on the two sides, being equal, by elementary dynamics (*l. c.* pp. 257–267), we obtain the equation

$$F(U, V)\,f(u, v) = F(U', V')\,f(u', v') ;$$

subject to the condition

$$M(U'^2 + V'^2) + m(u'^2 + v'^2) = M(U^2 + V^2) + m(u^2 + v^2).$$

The well-known solution of this functional equation is

$$\left.\begin{aligned} F(U, V) &= \text{Const. exp } -\lambda M(U^2 + V^2) \\ f(u, v) &= \text{Const. exp } -\lambda m(u^2 + v^2) \end{aligned}\right\} ;$$

where λ is a constant to be determined from the given mean energy of the system.

But if the independence of F and f is not assumed in the premisses, for $F(U,V)f(u,v)$ substitute $\psi(U,V,u,v)$; and, putting χ for $\log\psi$, solve the functional equation

$$\begin{aligned}\chi(U,V,u,v)-\chi(U',V',u',v')\\ +\lambda\{M(U^2+V^2)+m(u^2+v^2)\\ -M(U'^2+V'^2)-m(u'^2+v'^2)\}\equiv 0.\end{aligned}$$

Differentiating twice with regard to each of the variables U, V, u, v, we have

$$\left(\frac{d^2\chi}{dU^2}\right)=-2\lambda M=\left(\frac{d^2\chi}{dV^2}\right);\ \left(\frac{d^2\chi}{du^2}\right)=-2\lambda M=\frac{d^2\chi}{dv^2}.$$

Also $$\frac{d^2\chi}{dU\,dV}=0;\ \frac{d^2\chi}{du\,dv}=0.$$

Whence $\chi=\text{Const.}-\lambda\{M(U^2+V^2)+m(u^2+v^2)\}+$ a linear function of the variables, which disappears, if, as here generally, the mass-centre of the system is assumed to be at rest ; or otherwise can be adapted to uniform motion of the mass-centre (*l. c.* pp. 253, 257).

Next suppose that in addition to the motion of the masses there are internal movements designated by generalized co-ordinates. As above, the species and varieties of couples may be defined by the velocities of the mass-centres and the place of the point of impact on the contour (of one of the molecules). But that point does not now in general move in a right line parallel to the mass-centre ; not like the point of a lance at a tournament, but, rather, like a point on the edge of a sabre which the dragoon whirls as he charges. Collisions therefore will now be divided not only according to the velocities, the *classes* of the colliding molecules, but also according to the values of their generalized co-ordinates, their *genera* (*l. c.* p. 263). If now stability is defined as steady distribution of velocities for each particular set of values assumed by the co-ordinates, then we may reason as before that each variety of each class of each genus must remain equal in content to its reciprocal ; and therefore that the velocities must be distributed according to a normal law of error of which the variables are (squares and products of) velocities and the coefficients are functions of the co-ordinates. But if the steady distribution of the classes in each genus is not *implied* in the definition of stability, it may be *deduced* as before (*l. c.* p. 263) from the definition of stability as steady distribution of classes *on an average of all the distributions* in the medley.

When we pass to *encounters* the argument is not materially affected by the circumstances that the change of velocities is not now instantaneous, and that the reciprocal couple consists of different *genera* as well as classes. But it can now no longer be taken for granted that the differential factor of the frequency-content relating to any species of couple—of the form

$$\Delta Q_1 \Delta Q_2 \ldots \Delta U \Delta V \Delta \dot{Q}_1 \Delta \dot{Q}_2 \ldots \Delta q_1 \Delta q_2 \ldots \Delta u \Delta v \Delta \dot{q}_1 \Delta \dot{q}_2$$

(*l. c.* p. 267)—(where U, V, u, v are velocities of the mass-centres and the other symbols relate to generalized co-ordinates) retains its value unchanged after the change which is signified by affecting each of the above symbols with a dash. To secure the equality of the differential factors before and after an encounter, recourse must be had to the theorem of Liouville.

In general, in order that the distribution of velocities should be stable, it is necessary that it should obey the normal law of frequency in two forms: one form (proper to each genus) in which the coefficients of (the squares and products of) the velocities are functions of the co-ordinates, and another form (pertaining to the medley as a whole) in which the coefficients do not involve co-ordinates.

2. *Proof that the normal distribution is sufficient.*—To show that this distribution is sufficient, as well as necessary, recourse must be had to *à priori* probability (*l. c.* p. 257): the presumptions which attach to the hypothesis of random distribution. Of this kind is the generally admitted proposition that the frequency of a class is not altered by changing the signs of *all* the components of velocity of momentum (*l. c.* p. 266). Thus in the simple case first considered where the section (U, V; u, v)s passed by collision into (u', v'; U′, V′)s; the latter section is equal in content to the section designated by the same velocities with signs reversed, in our notation (−U′, −V′; −u', −v')s; the capital letters now preceding as the section is positive (consilient). By our third argument (and simple dynamics) the last written section passes by collision into (−u, −v; −U, −V)s; which is *à priori* equal to (U, V; u, v)s. Thus the content of the section first considered is the same at the end of the interval τ as it was at the beginning. The contents of this section and of every other section thus remain constantly the same if the normal law of frequency holds good. This proof may be transferred to the general case of several degrees of freedom more directly than appeared before (*l. c.* p. 265).

3. *Correlation.*—There is of course interdependence between molecules engaged in an *encounter*. Thus in the

simplified case of two dimensions, if U and u be the velocities prior to encounter let U_1, u_1 designate the velocities just after they have begun to influence each other sensibly; let U_2, u_2; $U_3, u_3 \ldots$ be the pairs at later stages; stages being measured by equal intervals of distance or, better, of time. Given the law of repulsion, we can (theoretically) calculate U_t and u_t the velocities at any time (say before that of least distance between the mass-centres) in terms of U, u, and t; and thence U, u in terms of U_t, u_t, and t. To obtain the correlation between U_t and u_t from the frequency-function of U and u, viz. Const. exp $-\lambda(MU^2+mu^2)$, it is proper to substitute for U and u their values in terms of U_t and u_t (we need not trouble about the differential factors, since, by Liouville's theorem $dU_t du_t = dU_t' du_t'$). There would result a complicated expression showing *interdependence* between the velocities at any assigned stage of the encounter, but not *normal correlation.* But if the *averages* of the velocities over the period of approach (or regression) are respectively ${}_1U$ and ${}_1u$, then between those variables there will be *normal* correlation (of the form (2)). (Cp. above (14) and reference). Correlation in this sense may be expected throughout that small part of the field which is occupied by molecules in encounter.

4. *Relations between the arguments.*—The third argument proves in one respect more, in another less, than the first. The third argument proves that *perfect* stability cannot exist unless the velocities of the mass-centres are distributed according to the normal law of frequency in its simplest form without terms implying correlation between those velocities (of the kind shown in (2)). The first argument cannot prove this; but it proves that normal distribution will be set up approximately at least in the medley. Whereas the *conditional* conclusion of the third argument does not by itself confer the power of prediction. Could data such as those which form the premisses of the third argument be supposed, and yet stability not result? Certainly a non-conservative system may be imagined, such that, in addition to the conservation of Momentum $MU+mu$ (in the case of one dimension), there should be secured the conservation—not of energy, but—of the quantity MU^4+mu^4. It might *primâ facie* be argued as above that the system could not be perfectly stable unless the velocities are distributed according to the law of frequency Const. exp $-(MU^4+mu^4)$. But there is not fulfilled the Liouville condition required by the third as well as the second argument (II. 3). The second method has an advantage over the others in the

readiness with which it is adapted to the case of external forces. We have only to put as the imposed condition the constancy—not of the kinetic energy as above throughout, but—of the total energy (Cp. Jeans, Phil. Mag. v. p. 617, 1903). Of course the acceleration must not be of such magnitude as to mask the random character of the molecular motion (Cp. Watson, 'Kinetic Theory of Gases,' p. 35). The second argument, however, is perhaps not so incontrovertible but that it may be indebted to the others for some corroboration. The three arguments are mutually complementary.

XXVI. *Method of Tracing Caustic Curves.*

By A. S. Percival, *M.A.*, *M.B. Camb.*[*]

A CAUSTIC CURVE is the locus of all the primary focal lines formed by the intersection of two contiguous reflected or refracted rays.

Many mathematicians have devoted their energies to the problem of discovering the general equation of a Caustic Curve, but without success as far as I know except in a few special cases. The method usually given in the books is first to find an expression for the refracted wave-front, which is a Cartesian oval, and then to find the evolute of this curve. This is a most tedious and laborious proceeding, but in this paper I submit a simple method which will enable one to trace the Caustic due to either reflexion or refraction at a single spherical surface with ease, expedition, and accuracy. As corresponding points can be marked off after refraction at another surface, the Caustic formed by a lens can be plotted out in a reasonable time.

Now different lenses show differently shaped Caustics, and it will be found that the general rules for the size and position of the Least Circle of Aberration are by no means true when a lens is used with its full aperture.

Refraction at a Single Spherical Surface.

Let S be the source of light ; consider the ray SP making an angle θ with the axis SCA, incident at P and refracted as PR. Let RP produced meet the axis at T. From C drop the perpendiculars CM and CN on the incident and refracted rays respectively.

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[*] Communicated by Professor J. W. Nicholson, F.R.S.

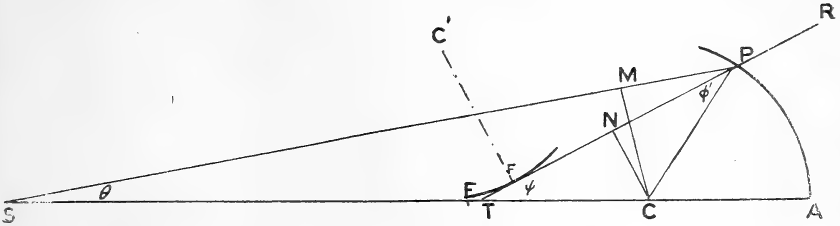
Let $CSP=\theta$, $SC=a$, $CP=r$,

$CPM=\phi$, $NP=n=r\cos\phi'$,

$CPN=\phi'$, $CN=p=r\sin\phi'$,

$CTP=\psi$, $CM=\mu p=r\sin\phi$.

Fig. 1.



$a=20$, $r=5$; $\mu=1{\cdot}523$.

θ.	ϕ.	ϕ'.	n.	p'.	fP.	p.	ρ.
0	0	0	5	5·5325	10·5325	0	0
10° 10′ 55″	−45°	−27° 39′ 50″	4·4284	3·5420	7·9704	−2·3214	4·9766

(i.) From the figure it is seen that $\psi=\theta+\phi-\phi'$.

(The magnitudes are considered as simple geometrical quantities without any vectorial sense of direction.)

Differentiate (i.) with regard to ψ.

$$1=\frac{d\theta}{d\psi}+\frac{d\phi}{d\psi}-\frac{d\phi'}{d\psi}. \tag{i'.}$$

But $\sin\theta=\frac{\mu p}{a}$, $\sin\phi=\frac{\mu p}{r}$, $\sin\phi'=\frac{p}{r}$.

$$\therefore\ \frac{d\theta}{d\psi}=\frac{\mu p'}{a}\sec\theta,\qquad \frac{d\phi}{d\psi}=\frac{\mu p'}{r}\sec\phi,\qquad \frac{d\phi'}{d\psi}=\frac{p'}{r}\sec\phi',$$

when $p'=\frac{dp}{d\psi}$.

$$\therefore\ \text{from (i'.)}\quad \frac{1}{p'}=\frac{\mu}{a}\sec\theta+\frac{\mu}{r}\sec\phi-\frac{1}{r}\sec\phi',\ \ .\ \ .\ \ . \tag{a}$$

$$\text{(ii)}\quad\text{or}\quad p'=\frac{ar}{\mu r\sec\theta+\mu a\sec\phi-a\sec\phi'}.$$

Differentiate (a) again with regard to ψ:

$$\frac{-p''}{p'^2}=\frac{\mu}{a}\sec^2\theta\sin\theta\frac{d\theta}{d\psi}+\frac{\mu}{r}\sec^2\phi\sin\phi\frac{d\phi}{d\psi}-\frac{1}{r}\sec^2\phi'\sin\phi'\frac{d\phi'}{d\psi}$$

$$=\frac{\mu}{a}\sec^3\theta\,\frac{\mu p}{a}\frac{\mu p'}{a}+\frac{\mu}{r}\sec^3\phi\,\frac{\mu p}{r}\frac{\mu p'}{r}-\frac{1}{r}\sec^3\phi'\frac{p}{r}\frac{p'}{r}.$$

$$\therefore\ \frac{p''}{p}=-\frac{p'^3}{a^3r^3}\left[\mu^3r^3\sec^3\theta+\mu^3a^3\sec^3\phi-a^3\sec^3\phi'\right].$$

(iii.) $$\rho=p+p''=p\left(1+\frac{p''}{p}\right)$$

$$=p\left[1-\frac{\mu^3r^3\sec^3\theta+\mu^3a^3\sec^3\phi-a^3\sec^3\phi'}{(\mu r\sec\theta+\mu a\sec\phi-a\sec\phi')^3}\right].$$

Now if C be regarded as the origin of the p, ψ equation to the Caustic (which it is unnecessary to find) as fNP is the tangent to the Caustic at the point f, and as $f\mathrm{N}=p'$ and $\mathrm{NP}=n$, the distance fP is given by $p'+n$ where $n=r\cos\phi'$. Hence any point f can be readily found on the Caustic and the radius of curvature at that point is given by (iii.).

On now introducing signs of direction so that the formulæ shall hold universally when the symbols carry signs of direction, it will be noted that in the diagram every magnitude is positive except ϕ, ϕ' and p or $r\sin\phi'$; consequently in (i.) the signs of ϕ and ϕ' must be reversed, and so we obtain

(1) $$\psi=\theta-\phi+\phi'.$$

It will be convenient to regard p as measured always in the direction CN, whatever that may be: for ρ (C$'f$ in fig. 1) the radius of curvature is always parallel to CN, and when ρ carries the same sign as p the radius is drawn in the same direction as CN, but when ρ carries a sign opposite to that of p it is drawn in the direction NC.

When the incident light presents a plane wave-front, $\theta=0$ and a becomes infinite, but in that case

$$\frac{1}{p'}=\frac{\mu}{a\cos 0}+\frac{\mu}{r}\sec\phi-\frac{\sec\phi'}{r},$$

so $$p'=\frac{r}{\mu\sec\phi-\sec\phi'}$$

and $$\rho=p\left\{1-\frac{\mu^3\sec^3\phi-\sec^3\phi'}{(\mu\sec\phi-\sec\phi')^3}\right\}.$$

If the Caustic by reflexion at a spherical surface be considered, we have only to substitute -1 for μ, and put $\phi=-\phi'$.

In the case of a plane wave-front ϕ must be taken as the variable.

In the general case when θ is given, $\sin\phi = -\frac{a}{r}\sin\theta$.

The formulæ for all cases can then be tabulated as below.

TABLE I.

$p = r\sin\phi'$, $n = r\cos\phi'$; $fP = n + p'$.

REFRACTION.	REFLEXION.
$\psi = \theta - \phi + \phi'$. $p' = \dfrac{ar}{\mu r\sec\theta + \mu a\sec\phi - a\sec\phi'}$. $\rho = p\left\{1 - \dfrac{\mu^3 r^3\sec^3\theta + \mu^3 a^3\sec^3\phi - a^3\sec^3\phi'}{(\mu r\sec\theta + \mu a\sec\phi - a\sec\phi')^3}\right\}$.	$\psi = \theta + 2\phi'$. $p' = \dfrac{-ar}{r\sec\theta + 2a\sec\phi'}$. $\rho = p\left\{1 - \dfrac{r^3\sec^3\theta + 2a^3\sec^3\phi'}{(r\sec\theta + 2a\sec\phi')^3}\right\}$.
Plane Wave-front.	Plane Wave-front.
$\psi = \phi' - \phi$. $p' = \dfrac{r}{\mu\sec\phi - \sec\phi'}$. $\rho = p\left\{1 - \dfrac{\mu^3\sec^3\phi - \sec^3\phi'}{(\mu\sec\phi - \sec\phi')^3}\right\}$	$\psi = 2\phi'$. $p' = \dfrac{-r}{2\sec\phi'} = -\frac{1}{2}n, \quad \therefore fP = \frac{1}{2}n$. $\rho = p\left\{1 - \dfrac{2\sec^3\phi'}{(2\sec\phi')^3}\right\} = \frac{3}{4}p$.

Some hesitation may be felt in accepting these results without further examination; but all doubts will be removed on showing that fP as here obtained is identical with v_1 as given in the usual formula :—

$$\frac{\mu\cos^2\phi'}{v_1} - \frac{\cos^2\phi}{u} = \frac{\mu\cos\phi' - \cos\phi}{r}$$

or

$$v_1 = \frac{\mu ur\cos^2\phi'}{u(\mu\cos\phi' - \cos\phi) + r\cos^2\phi}.$$

On referring to fig. 1, SP or u is seen to be $r\cos\phi + a\cos\theta$.

$$\begin{aligned} fP &= r\cos\phi' + \frac{ar}{\mu r\sec\theta + \mu a\sec\phi - a\sec\phi'} \\ &= \frac{\mu r^2\cos\phi'\sec\theta + \mu ar\cos\phi'\sec\phi}{\mu r\sec\theta + \mu a\sec\phi - a\sec\phi'} \\ &= \frac{\mu r^2\cos^2\phi'\cos\phi + \mu ar\cos^2\phi'\cos\theta}{\mu r\cos\phi\cos\phi' + \mu a\cos\theta\cos\phi' - a\cos\theta\cos\phi} \\ &= \frac{\mu ur\cos^2\phi'}{u\mu\cos\phi' + r\cos^2\phi - u\cos\phi} \equiv v_1. \end{aligned}$$

Whenever $\rho=0$, there is either a cusp, as at the point F in figs. 1, 2, 4, etc., or there is a stationary point (*point d'arrêt*) as L in fig. 4, where the angle of incidence is the critical angle and total reflexion occurs at all greater angles of incidence.

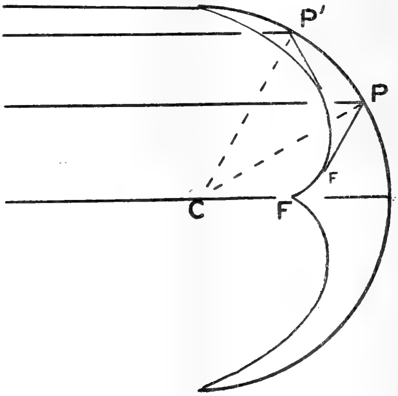
When the path of light is from the dense towards the rare medium $\frac{1}{\mu}$ must be substituted for μ in the given equations, as has been done in the planoconvex lens represented in fig. 4.

Beneath fig. 1 is a table of all the values required for finding the position of the first focal lines when the angle of incidence is 0, and 45°. SC or a is assumed to be 20, and r 5 units, while μ, as in all cases, is taken to be 1·523 which is the ordinary value of μ in American spectacle glass.

Reflexion at a Spherical Surface.

As a simple example fig. 2 is given, which represents the reflexion of a plane wave-front at a spherical surface where $r=5$. The adjoining table corresponding to four values of ϕ' is sufficient to trace the entire caustic in three minutes. The

Fig. 2.



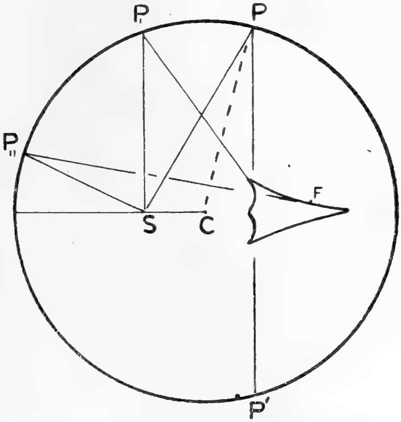
Reflexion. Plane Wave-front. $r=5$.

ϕ'.	$fP=\frac{1}{2}n$.	$\rho=\frac{3}{4}p$.
0	2·5	0
30°	2·165	1·875
60°	1·75	3·247
90°	0	3·75

advantage of being given ρ is seen, as by the direction of the curve one can tell whether it is necessary to find any more intermediate values of fP.

It will be found that if $a \overset{=}{<} \frac{r}{3}$, and if one reflexion occurs at each point of the circle, there will be four cusps, all within the circle, as shown in fig. 3 where $a=1{\cdot}5$ and $r=5$. The table below the diagram gives all the values required.

Fig. 3.



$a=1{\cdot}5$, $r=5$.

θ.	ϕ'.	n.	p'.	fP.	p.	ρ.
0	0	5	$-{\cdot}9375$	4·0625	0	0
59° 54′ 38″	15° 2′ 41″	4·8286	$-{\cdot}5734$	4·2552	1·2979	·4466
90°	17° 27′ 27″	4·7697	0	4·7697	1·5	0
155°	7° 17′ 2″	4·9597	3·0090	7·9687	·6339	$-5{\cdot}9571$
180°	0	5	3·75	8·75	0	0

It is advisable in cases of reflexion as in fig. 3 to tabulate the values when $\psi=90°$, for the reflected ray PP′ in that case marks the boundary of the caustic in one direction.

When $\psi=90°$, θ and ϕ are easily found, for

$$\sin\phi=-\frac{a}{r}\sin\theta, \quad \text{and} \quad 2\phi'=90°-\theta,$$

$$2\sin^2\phi=1-\cos 2\phi'=1-\sin\theta,$$

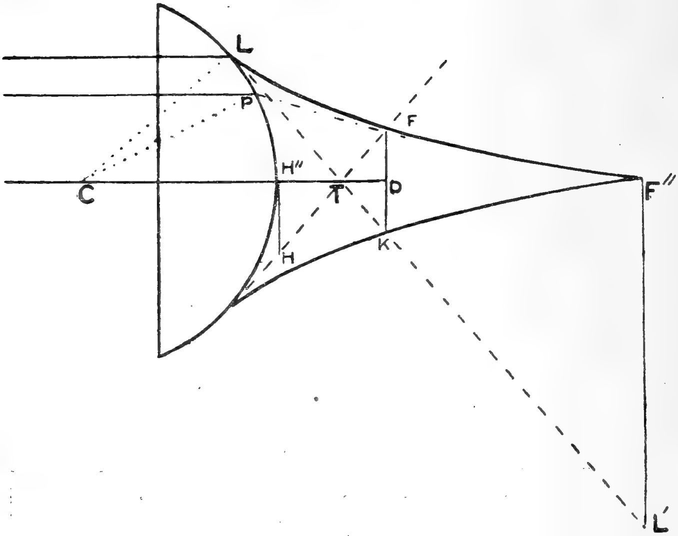
$$2a^2\sin^2\theta+r^2\sin\theta-r^2=0.$$

The solution of this quadratic gives $\sin\theta$, and $\sin\phi=-\frac{a}{r}\sin\theta$.

Refraction at a Spherical Surface.

Fig. 4 represents a plane wave-front incident on a plano-convex lens of radius 5 and thickness 3. As refraction only occurs at the spherical surface where the light encounters the rare medium, $\frac{1}{\mu}$ must replace μ in the given equations. The critical angle when $\mu=1{\cdot}523$ is 41° 2′ 27·6″, so this is the maximum value of ϕ, and the three values for the three angles ϕ' (0, −45°, −90°) given in the table are sufficient to trace the caustic. It will be noticed that at F″ and at L $\rho=0$, F″ being a cusp and L being a *point d'arrêt*.

Fig. 4.



Refraction. Plane Wave-front. $r=5$, $\mu=1{\cdot}523$.

ϕ.	ϕ'.	n.	p'.	fP.	p.	ρ.
0	0	5	−14·5602	−9·5602	0	0
−27° 39′ 50″	−45°	3·5355	− 7·4308	−3·8953	−3·5355	24·5613
−41° 2′ 28″	−90°	0	0	0	−5	0

Least Circle of Aberration.

The extreme ray LTKL′ cuts the axis at T and the caustic at K; D marks the position of the Least Circle and DK or

k its radius ; F″T is the longitudinal aberration (usually denoted by a) and F″L′ is the lateral aberration denoted by l. Now in the books it is said that F″D may be taken as $\frac{3}{4}a$ or $\frac{3}{4}$F″T, and k as $\frac{1}{4}l$. In this case the distance F″D of the Least Circle from F″ is about $\frac{5}{6}$F″T and k is about $\frac{1}{6}l$. This example is sufficient to show that this simple rule cannot be relied upon when a lens is used with its full aperture. In most cases it will be sufficient to find fP when ϕ' is midway between 0 and its extreme limit and the value of ρ at the point f ; K, the intersection of the extreme ray with the small arc drawn through f, will enable one to determine the size and position of the Least Circle with a high degree of accuracy.

In the diagram H″H represents the second Principal Plane cutting the extreme ray at H, and the angle H″TL or DTK is ψ or $\phi'-\phi$, *i.e.* $-48° 57′ 32″$. Indeed the angles DTF and H″TH are geometrically equal to ψ, though they are measured in the reverse direction.

Clearly from the diagram

(1) a or $\text{F}''\text{T}=\text{F}''\text{H}''-\text{TH}''=\text{F}''\text{H}''-\text{H}''\text{H} \cot \text{H}''\text{TH}$
$=f''-y \cot \psi$, where $y=\text{H}''\text{H}$.

(2) l or $\text{F}''\text{L}'=\text{TF}'' \tan \text{F}''\text{TL}'=a \tan \psi$.

(3) k or $\text{DK}=\text{TD} \tan \text{DTK}=\text{TD} \tan \psi$.

Now (2) and (3) give the correct numerical result which is all that is required for l and k, for they are essentially signless ; in (1), however, it is necessary to know whether a is positive or negative. A moment's consideration will show that (1) is universally true when the symbols carry signs of direction, for as H″H is negative and H″TH is positive, every term in the equation carries the same (negative) sign.

In order then to determine a and l it is only necessary to trace the extreme ray, but to find the size and position of the Least Circle it is necessary to trace that part of the caustic which the extreme ray cuts.

The caustic in fig. 4 is extraordinarily large as it even extends beyond the Principal Plane, although the aperture of the lens is relatively small. A much smaller caustic is formed by the same lens if its position is reversed as in fig. 8, where the semiaperture of the lens is far greater. If, however, the source of light be at or near the first principal focus of the planoconvex, so that the incident light is a widely divergent cone, this position of the lens with its plane surface facing the incident light gives far the smaller caustic.

Before dealing with such a case, or with that of the plane wave-front in fig. 8, it will be necessary to consider refraction at a plane surface.

Refraction at a Plane Surface.

Let OP be the plane surface and OT the initial line normal to it, on which is situated the source S (fig. 5).

Let SP incident at P be refracted as PR, where $\phi = \text{LPS}$ or OSP, and $\phi' = \text{LPN} = \text{OTP} = \text{PON}$, and let ON or p be perpendicular to PT.

Then if $\text{SO} = b$, $p = \text{OP} \cos \phi' = b \tan \phi \cos \phi'$ and n or $\text{NP} = \text{OP} \sin \phi' = b \tan \phi \sin \phi'$.

As ϕ' now replaces ψ, p' is obtained by differentiating p with regard to ϕ'.

$$p' = b\left(\cos \phi' \sec^2 \phi \frac{d\phi}{d\phi'} - \tan \phi \sin \phi'\right).$$

But as $\sin \phi = \mu \sin \phi'$, $\qquad \dfrac{d\phi}{d\phi'} = \mu \sec \phi \cos \phi'$,

so $\quad p' = b(\mu \sec^3 \phi \cos^2 \phi' - \tan \phi \sin \phi')$,

and
$$p'' = b\left[3\mu \cos^2 \phi' \sec^3 \phi \tan \phi \frac{d\phi}{d\phi'} - 2\mu \sec^3 \phi \cos \phi' \sin \phi - \sin \phi' \sec^2 \phi \frac{d\phi}{d\phi'} - \tan \phi \cos \phi'\right]$$
$$= b(3\mu^2 \cos^3 \phi' \sec^4 \phi \tan \phi - 3 \cos \phi' \sec^2 \phi \tan \phi - \tan \phi \cos \phi'),$$
$$\rho = p + p'' = b \tan \phi \cos \phi' (1 + 3\mu^2 \cos^2 \phi' \sec^4 \phi - 3 \sec^2 \phi - 1)$$
$$= 3b \tan \phi \cos \phi' \sec^2 \phi (\mu^2 \sec^2 \phi \cos^2 \phi' - 1),$$

or $\qquad 3p \sec^2 \phi\, (\mu^2 \sec^2 \phi \cos^2 \phi' - 1)$.

As before fNP is the tangent to the caustic at the point f, and $f\text{P} = f\text{N} + \text{NP} = p' + n$, and as all the magnitudes in the diagram (b, ϕ, ϕ') are of the same sign, the formulæ tabulated below are universally correct when signs of direction are introduced.

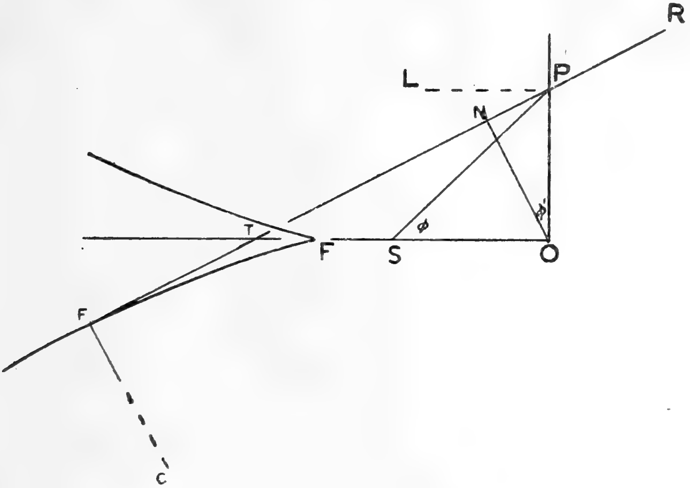
TABLE II.

Refraction at a plane surface.

$p = b \tan \phi \cos \phi'$.	$f\text{P} = b\mu \sec^3 \phi \cos^2 \phi'$.
$n = b \tan \phi \sin \phi'$.	$\rho = 3p \sec^2 \phi (\mu^2 \sec^2 \phi \cos^2 \phi' - 1)$.

In fig. 5 it will be noticed that as before when p and ρ carry the same sign Cf is measured in the same direction as ON. When $\phi=45°$ ρ is more than 56, so C′ is beyond the limits of the diagram in the direction f C.

Fig. 5.



Refraction at a plane surface.

SO$=b=4$: $\mu=1{\cdot}523$.

ϕ.	ϕ'.	fP.	p.	ρ.
0	0	6·092	0	0
45°	27° 39′ 50″	13·5165	3·5427	56·0971

Caustic formed by a Lens.

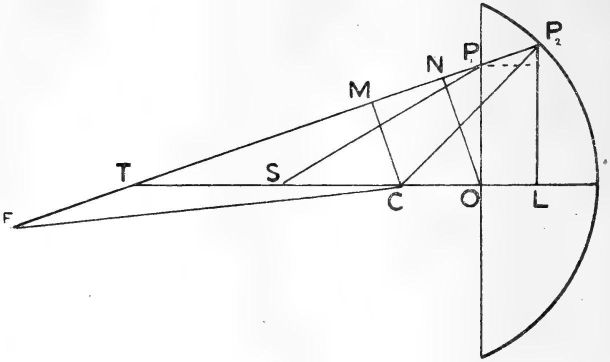
In all cases it is necessary to know the axial thickness (t), the curvature of each surface, and the distance of the radiant point either from the proximal surface or from its centre of curvature. Formulæ must then be obtained to determine in terms of the data the length of the path (P_1P_2) of any ray within the lens, and the angle of incidence at each surface.

We will consider first plano lenses.

A (1) *The plane surface facing the incident light.*

Fig. 6 represents a radiant point S on the axis of a plano-convex lens. It will be necessary to find the values of fP_1 and p_1 (due to the refraction at the plane surface) for the axial and the extreme rays and one or two intermediate rays by the previous method. To avoid confusion in the diagram fP_1 has been made greater than its real length for this angle of incidence.

Fig. 6.



Produce fP_1 to P_2 on the curved surface of the lens, draw P_2L perpendicular to the axis SCO, and let CM and ON (or p_1) meet fTP_2 at right angles; join fC and CP_2.

The point f is the radiant point for the second surface, fC is the part of the initial line that is represented by SC or a in fig. 1, and CP_2f or ϕ_2 is the angle of incidence, and CfP_2 or θ_2 is the angle which fP_2 makes with the new initial line. As in fig. 5, $SO=b$, $ON=p_1$, $OSP_1=\phi_1$, and $OTP_2=\phi_1'$.

From fig. 6 it is readily seen that

(i.) $CM = r\sin\phi_2 = TC\sin\phi_1' = (TO-CO)\sin\phi_1'$
$= (b\tan\phi_1\cot\phi_1' - r + t)\sin\phi_1'$.

∴ $r\sin\phi_2 = b\tan\phi_1\cos\phi_1' + (t-r)\sin\phi_1'$
or $p_1 + (t-r)\sin\phi_1'$.

(ii.) $P_1P_2\cos\phi_1' = OL = t - r\operatorname{vers}(\phi_1'+\phi_2)$.

(iii.) $\tan\theta_2 = \dfrac{CM}{fM} = \dfrac{r\sin\phi_2}{fP_1 + P_1P_2 - r\cos\phi_2}$.

(iv.) fC or $a_2 = fM\sec\theta_2 = (fP_2 - r\cos\phi_2)\sec\theta_2$.

In the diagram all the magnitudes are positive except ϕ_2, so to make the formulæ of universal application when direction-signs are added it is only necessary to change the sign of ϕ_2 as has been done in the table. It has been shown in fig. 4 with what extreme simplicity the caustic can be traced when the light presents a plane wave-front with normal incidence. If the plane wave-front be incident at an angle α on the plane surface and refracted at an angle α', the initial line for the spherical surface will make an angle

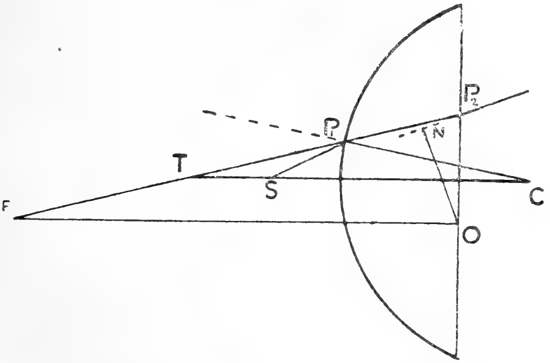
α' with the axis of the lens. The caustic will appear as if rotated about C through the angle α' from the axis of the lens. If the emergent light be received on a small vertical screen, the flare of light seen on it is of course the coma.

The difficult subject of coma can be simply introduced to the student by getting him to trace the caustic of such a lens due to a plane wave-front incident at some angle α. With the help of the table below fig. 4 it can be done in three or four minutes. On then drawing a vertical line through the cusp, parallel to the plane surface of the lens, he will find that the rays, which are symmetrical above and below the axis of the lens, when produced beyond the caustic will intersect on this vertical line below the cusp if α be positive. This vertical line presents an edge view of the intersecting comatic circles that produce the flare below the cusp.

A (2) *The curved surface facing the incident light.*

The construction of fig. 7 requires no explanation; S is the radiant point, $SC=a$, $\sin\phi_1=-\frac{a}{r}\sin\theta_1$ as before, and fP_1 is found by Table I. As the second surface is plane fO represents SO in fig. 5 or b in Table II.; since f is the radiant point for the second surface, its angle of incidence is $\phi_2=CTP_2$ (or $OfP_2)=\theta_1-\phi_1+\phi_1'$.

Fig. 7.



It is required to find P_1P_2 and fO in terms of the known quantities. From the diagram it is obvious that

$$P_1P_2\cos\phi_2=t-r\,\text{vers}\,(\phi_1-\theta_1),$$

and $$fO \text{ or } b=fP_2\cos\phi_2.$$

In the figure all the magnitudes are positive except r, so the sign of r must be changed in the above to give the general formulæ in Table III. (V is not shown.)

TABLE III. (Plano lenses.)

(1) First surface plane ; as in fig. 5. $SO=b$; $OSP_1=\phi_1$; $OTP_1=\phi_1'$.

(i.) $$p_1=b\tan\phi_1\cos\phi_1'.$$

(ii.) $$fP_1=b\frac{\mu\cos^2\phi_1'}{\cos^3\phi_1}.$$

Second surface.

(1) $$\sin\phi_2=\frac{1}{r}(\overline{r-t}\sin\phi_1'-p_1).$$

(2) $$P_1P_2=\frac{t-r\operatorname{vers}(\phi_1'-\phi_2)}{\cos\phi_1'}.$$

(3) $$\tan\theta_2=\frac{r\sin\phi_2}{r\cos\phi_2-fP_2}.$$

(4) $$a_2 \text{ or } fC=(fP_2-r\cos\phi_2)\sec\theta_2.$$

Plane Wave-front.
Incidence Normal.

$$v=r\cos\phi'+\frac{\mu r}{\sec\phi-\mu\sec\phi'}.$$

$$\rho=r\sin\phi'\left\{1-\frac{\sec^3\phi-\mu^3\sec^3\phi'}{(\sec\phi-\mu\sec\phi')^3}\right\}.$$

(I.) $$VP_2 \text{ or } v=r\cos\phi_2'+\frac{\mu a_2 r}{r\sec\theta_2+a_2\sec\phi_2-\mu a_2\sec\phi_2'}.$$

(II.) $$\rho=r\sin\phi_2'\left\{1-\frac{(r\sec\theta_2)^3+(a_2\sec\phi_2)^3-(\mu a_2\sec\phi_2')^3}{(r\sec\theta_2+a_2\sec\phi_2-\mu a_2\sec\phi_2')^3}\right\}.$$

(2) First surface curved ; as in fig. 1. $SC=a$, $C'PS=\phi_1$, $C'PT=\phi_1'$.

(i.) $$\sin\phi_1=-\frac{a}{r}\sin\theta.$$

(ii.) $$fP_1=r\cos\phi_1'+\frac{ar}{\mu r\sec\theta+\mu a\sec\phi-a\sec\phi'}.$$

Second surface.

(1) $$\phi_2=\theta_2=\theta_1-\phi_1+\phi_1'.$$

(2) $$P_1P_2=\frac{t+r\operatorname{vers}(\phi_1-\theta_1)}{\cos\phi_2}.$$

(3) $$p_2=fP_2\sin\phi_2\cos\phi_2'.$$

(I.) $$VP_2 \text{ or } v=fP_2\frac{\cos^2\phi_2'}{\mu\cos^2\phi_2}.$$

(II.) $$\rho=\frac{3p_2}{\cos^2\phi_2}\left\{\frac{\cos^2\phi_2'}{(\mu\cos\phi_2)^2}-1\right\}.$$

Plane Wave-front.
Incidence Normal.

First Surface.

(i.) $$fP_1=\frac{\mu r\cos^2\phi_1'}{\mu\cos\phi_1'-\cos\phi_1}.$$

Second Surface.

(1) $$\phi_2=\phi_1'-\phi_1.$$

(2) $$P_1P_2=\frac{t+r\operatorname{vers}\phi_1}{\cos\phi_2}.$$

(3) $$p_2=fP_2\sin\phi_2\cos\phi_2'.$$

(I.) $$v=fP_2\frac{\cos^2\phi_2'}{\mu\cos^2\phi_2}.$$

(II.) $$\rho=\frac{3p_2}{\cos^2\phi_2}\left\{\frac{\cos^2\phi_2'}{(\mu\cos\phi_2)^2}-1\right\}.$$

On substituting fO for b in Table II. we get

$$\mathrm{ON} \text{ or } p_2 = f\mathrm{P}_2 \sin\phi_2 \cos\phi_2',$$

$$\mathrm{VP}_2 \text{ or } v = f\mathrm{P}_2 \frac{\cos^2\phi_2'}{\mu\cos^2\phi_2},$$

$$\rho = \frac{3p_2}{\cos^2\phi_2}\left\{\frac{\cos^2\phi_2'}{\mu^2\cos^2\phi_2} - 1\right\}.$$

It should be noted that in tracing the caustic of a lens all the angles are required, for the first surface only $f\mathrm{P}_1$ and sometimes p_1, but for the second surface VP_2 and ρ are necessary.

It will be noticed that the usual form for finding the first focal line ($f\mathrm{P}_1$) has been given for a plane wave-front as this is speedier for logarithmic calculation; when a is finite and given, the method now suggested is the speedier, for a troublesome preliminary determination of u in terms of a, r, and ϕ_1, must be made before the usual method can be applied.

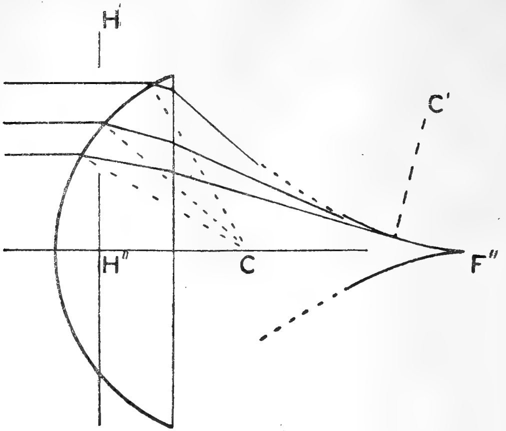
As an example of class A (2) the caustic is drawn of a plane wave-front incident upon the convex surface of the same planoconvex illustrated in fig. 4. The caustic in fig. 8 in full lines is due to this lens when stopped down to be of the same aperture as the lens in fig. 4, *i. e.*, when $\phi_1 = 41° 2' 28''$; the focal length $\mathrm{F''H''} = -9{\cdot}5602$ in each. It is immediately apparent what an advantage is gained by letting the curved surface face an incident plane wave-front. Indeed, if the aperture be increased to admit rays whose incident angle is 60° or even more, the caustic is still much smaller than that shown in fig. 4.

All the lines which it is necessary to draw are indicated on the diagram; a set square will indicate the perpendicular (p_2) from 0 on an emergent ray, and $\mathrm{C}'v$ is drawn parallel to p_2, its direction and length being given by the sign and figures under ρ in the explanatory table beneath fig. 8.

B. *The Bispherical Lens.*

The construction of fig. 9 (p. 273) requires little explanation: $\mathrm{C}_1\mathrm{P}_1$ is the radius of the first surface, $\mathrm{C}_2\mathrm{P}_2$ that of the second; $\mathrm{LSP}_1 = \theta_1$, $\mathrm{C}_1\mathrm{P}_1\mathrm{S} = \phi_1$, $\mathrm{C}_1\mathrm{P}_1\mathrm{T} = \phi_1'$, $\mathrm{C}_2\mathrm{P}_2\mathrm{T} = \phi_2$, $\mathrm{C}_2 f\mathrm{N} = \theta_2$, $\mathrm{C}_1\mathrm{MM}'$ and $\mathrm{C}_2\mathrm{N}$ are each at right angles to $\mathrm{P}_2\mathrm{P}_1\mathrm{TM}$.

Fig. 8.



Refraction of a plane wave-front by a planoconvex lens.

$$r=-5,\ t=3.\quad H_2O=\frac{t}{\mu}=\frac{3}{1{\cdot}523}=1{\cdot}9698.$$

ϕ_1.	ϕ_1'	fP_1.	ϕ_2.	ϕ_2'.	P_1P_2.
0	0	−14·5602	0	0	3
30°	19° 9′ 56″	−11·8685	−10° 50′ 4″	−16° 38′ 9″	−2·3724
41° 2′ 28″	25° 32′ 20″	−10·0001	−15° 30′ 8″	−24° 1′ 13″	−1·8380
60°	34° 39′ 17″	−6·8447	−25° 20′ 43″	−40° 41′ 20″	− ·5532

fP_2.	p_2.	v.	ρ.
−11·5602	0	−7·5904	0
−9·4961	1·7103	−5·9337	−3·1366
−8·1621	1·9925	−4·8151	−3·9438
−6·2915	2·0421	−2·9081	−5·2245

The geometry of fig. 9 shows that

(i.) $\sin C_1P_1S=\frac{a_1}{r_1}\sin C_1SP_1$, or $\sin\phi_1=\frac{a}{r}\sin\theta_1$;

(ii.) $C_2N=M'C_1-MC_1=C_1C_2\sin C_1C_2M'-C_1P_1\sin C_1P_1M$,

and as $C_1C_2M'=C_2TP_1=\theta_1-\phi_1+\phi_1'$,

$$r_2\sin\phi_2=(r_1+t-r_2)\sin(\theta_1-\phi_1+\phi_1')-r_1\sin\phi_1' ;$$

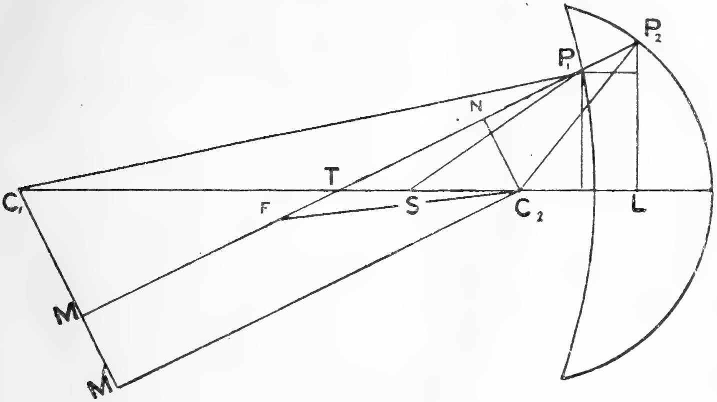
(iii.) $P_1P_2\sin C_2TP_2=C_2P_2\sin LC_2P_2-C_1P_1\sin SC_1P_1$:

$$\text{or}\quad P_1P_2\sin(\theta_1-\phi_1+\phi_1')=r_2\sin(\phi_2+\theta_1-\phi_1+\phi_1')$$
$$-r_1\sin(\theta_1-\phi_1) ;$$

(iv.) $$\tan\theta_2 = \frac{C_2N}{fN} = \frac{r_2\sin\phi_2}{fP_1 + P_1P_2 - r_2\cos\phi_2};$$

(v.) $$fC_2 \quad \text{or} \quad a_2 = C_2N \operatorname{cosec}\theta_2.$$

Fig. 9.



In the diagram all the magnitudes are positive except a_1 (or SC_1) and ϕ_2, so the signs of these symbols must be changed in order to make the above formulæ universally true when the symbols cary direction signs.

For a plane wave-front at normal incidence θ_1 and a_1 do not appear. These changes have been made in Table IV.

In fig. 10 an example is given of a biconvex lens of the same power as that of the previous planoconvex; in this case $r_2 = -r_1 = 9{\cdot}4552$ and, as can be readily found, the second principal plane passes through the point H″ where $H''B = 1{\cdot}0416$. From the table of values below the diagram it is seen that when $\phi_1 = 0$ and a or fC_2 (*i.e.* $fP_2 - r_2$) is $-33{\cdot}9892$, v or $F''B = -8{\cdot}5186$, and therefore $F''H'' = -9{\cdot}5602$ as in the case of the planoconvex in fig. 4 and in fig. 9.

The symmetrical biconvex gives the smallest caustic when the lens is midway between the object and its real image. Fig. 10 represents the case when parallel rays are incident; if provided with a diaphragm to reduce its aperture to that of the planoconvex in fig. 4 the caustic is fairly small, as is shown by the full lines. Even when used with its full aperture the caustic does not quite touch the surface of the lens.

Table IV. (Bispherical Lens.)

First Surface.

(i.) $\sin\phi_1 = -\frac{a_1}{r_1}\sin\theta_1$.

(ii.) $f\mathrm{P}_1 = r_1\cos\phi_1' + \frac{a_1 r_1}{\mu r_1\sec\theta_1 + \mu a_1\sec\phi_1 - a_1\sec\phi_1'}$.

Second Surface.

(1) $\sin\phi_2 = \frac{1}{r_2}\left\{(r_1+t-r_2)\sin(\phi_1-\phi_1'-\theta_1)+r_1\sin\phi_1'\right\}$.

(2) $\mathrm{P}_1\mathrm{P}_2 = \frac{r_2\sin(\phi_1-\phi_1'+\phi_2-\theta_1)-r_1\sin(\phi_1-\theta_1)}{\sin(\phi_1-\phi_1'-\theta_1)}$.

(3) $\tan\theta_2 = \frac{r_2\sin\phi_2}{r_2\cos\phi_2 - f\mathrm{P}_2}$.

(4) $f\mathrm{C}_2$ or $a_2 = -r_2\sin\phi_2\operatorname{cosec}\theta_2$.

(5) $p_2 = -r_2\sin\phi_2'$.

(I.) VP_2 or $v = r_2\cos\phi_2' + \frac{\mu a_2 r_2}{r_2\sec\theta_2 + a_2\sec\phi_2 - \mu a_2\sec\phi_2'}$.

(II.) $\rho = p_2\left\{1 - \frac{(r_2\sec\theta_2)^3 + (a_2\sec\phi_2)^3 - (\mu a_2\sec\phi_2')^3}{(r_2\sec\theta_2 + a_2\sec\phi_2 - \mu a_2\sec\phi_2')^3}\right\}$.

PLANE WAVE-FRONT: INCIDENCE NORMAL: θ_1 and a_1 do not appear.

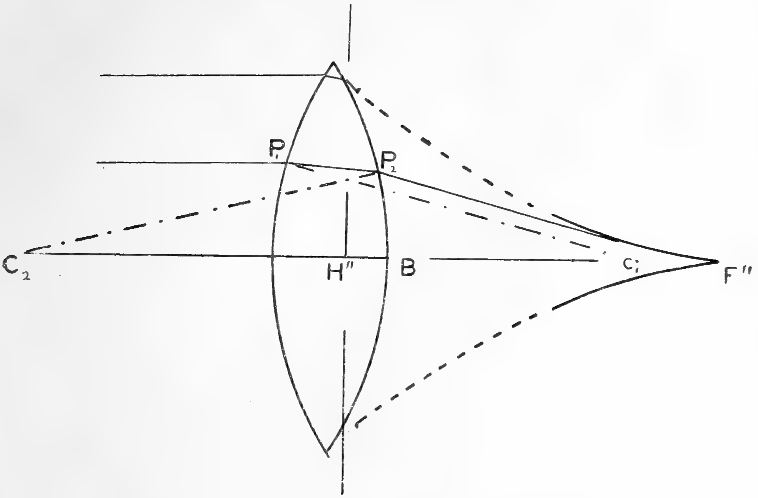
(i.) $f\mathrm{P}_1 = r_1\cos\phi_1' + \frac{r_1}{\mu\sec\phi_1 - \sec\phi_1'}$; or $\frac{\mu r_1\cos^2\phi_1'}{\mu\cos\phi_1' - \cos\phi_1}$.

(1) $\sin\phi_2 = \frac{1}{r_2}\left\{(r_1+t-r_2)\sin(\phi_1-\phi_1')+r_1\sin\phi_1'\right\}$.

(2) $\mathrm{P}_1\mathrm{P}_2 = \frac{r_2\sin(\phi_1-\phi_1'+\phi_2)-r_1\sin\phi_1}{\sin(\phi_1-\phi_1')}$.

The remaining formulæ remain unaltered.

Fig. 10.



Refraction of a plane wave-front by a biconvex lens.
$r=-9{\cdot}4552$; $r_2=9{\cdot}4552$; $t=3$; $\mu=1{\cdot}523$.

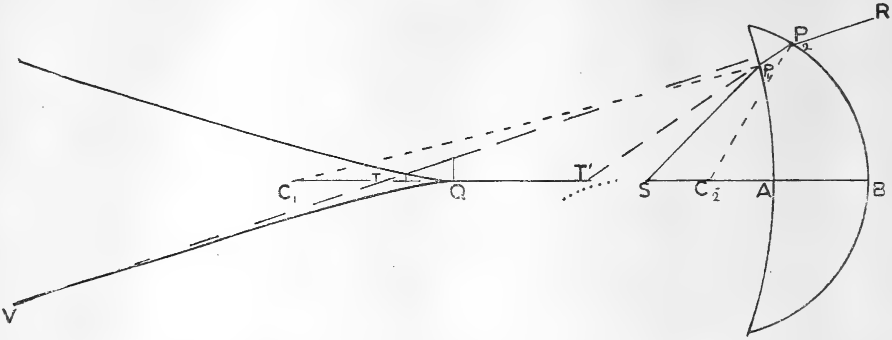
ϕ_1.	ϕ_1'.	$f\mathrm{P}_1$.	ϕ_2.	ϕ_2'.	$\mathrm{P}_1\mathrm{P}_2$.
0	0	−27·534	0	0	3
15°	9° 47′ 4″	−26·1429	−18° 50′ 19″	−29° 27′ 28″	2·4207
30°	19° 9′ 56″	−22·4396	−40° 9′ 55″	−79° 12′ 45″	·5098

$f\mathrm{P}_2$.	θ_2.	a_2.	v.	p_2.	ρ.
−24·534	0	−33·9892	−8·5186	0	0
−23·7222	− 5° 20′ 20″	−32·8131	−6·4323	4·6499	−16·0049
−21·9298	−11° 48′ 52″	−29·7865	− ·2435	9·2881	− 8·3388

The virtual caustic in fig. 11 is interesting. To avoid confusion in the diagram only the lines which have a relation to the extreme ray SP_1 are indicated ; $\mathrm{ASP}_1=\theta_1$ or 45°, $\mathrm{C}_1\mathrm{P}_1\mathrm{S}=\phi_1$, $\mathrm{C}_1\mathrm{P}_1\mathrm{T}'=\phi_1'$, and $\mathrm{P}_1\mathrm{P}_2$ is the path of the refracted ray through the lens, and of course the angle $\mathrm{AT}'\mathrm{P}_1=\psi_1$ or $\theta_1-\phi_1+\phi_1'$. It will be noted that if $\mathrm{P}_1\mathrm{T}'$ be produced it will touch the end of the caustic in dotted lines of which the lower limb only has been drawn ; this is the caustic formed by the first refraction. For the second refraction $\mathrm{C}_2\mathrm{P}_2\mathrm{T}'$ is

ϕ_2, and C_2P_2T is ϕ_2'. The line P_2T meets the final caustic at V.

Fig. 11.



Virtual Caustic formed by a meniscus where SA=4, and $r_1=15$; $r_2=5$; $a_1=-11$; $t=3$; $\mu=1{\cdot}523$.

θ_1.	ϕ_1.	ϕ_1'.	fP_1.	ϕ_2.	ϕ_2'.
0	0	0	5·3464	0	0
30°	21° 30′ 37″	13° 55′ 50″	6·1856	−15° 37′ 38″	−24° 13′ 17″
45°	31° 14′ 5″	19° 54′ 21″	7·3463	−24° 50′ 22″	−39° 46′ 31″

P_1P_2.	fP_2.	θ_2.	a_2.	v.	p_2.	ρ.
3	8 3464	0	3·3464	12·8411	0	0
2·2735	8·4590	20° 17′ 10″	3·8848	14·7693	2·0513	6·6197
1·2527	8·5985	27° 20′ 52″	4·5721	25·5068	3·1989	3·4034

Now although this caustic is very large, as Q is the conjugate focus of S, the longitudinal aberration is very small being only QT, while the lateral aberration is the short vertical line above Q, and the radius of the least circle of aberration is indicated by the minute vertical line between Q and T. If an eye, or a camera of very small aperture, were placed behind the lens in the direction P_2R and were focussed for the point V, the radiant point S would be represented by a focal line at right angles to the plane of the paper, but if placed in the direction AB and if focussed for the point Q, S would appear as a minute circle.

It has been previously pointed out that in most cases it is advisable to determine the angle ψ_2 or BTP_2. From the figure it is seen that

$$BC_2P_2 = BTP_2 + C_2P_2T = AT'P_2 + C_2P_2T'$$

$$\text{or} \qquad \psi_2 + \phi_2' = \psi_1 + \phi_2.$$

But $\psi_1 = \theta_1 - \phi_1 + \phi_1'$.

$\therefore$ $\psi_2 = \theta_1 - \phi_1 + \phi_1' + \phi_2 - \phi_2'$.

In the figure ϕ_2 and ϕ_2' only are negative, so the general formula when the symbols carry direction signs becomes

$$\psi_2 = \theta - \phi_1 + \phi_1' - \phi_2 + \phi_2'.$$

When the incident light is a plane wave-front at normal incidence, the formula is simply

$$\psi_2 = -\phi_1 + \phi_1' - \phi_2 + \phi_2'.$$

"Westward," Tankerville Terrace,
Newcastle-upon-Tyne.

XXVII. *The Forced Convection of Heat from a Pair of fine heated Wires.* By J. S. G. Thomas, *D.Sc. (Lond.), B.Sc. (Wales), A.R.C.S., A.I.C., Senior Physicist, South Metropolitan Gas Company, London* [*].

Introduction.

IN a recent communication [†], attention was directed to certain characteristics of the forced convection of heat from a pair of heated wires immersed in a slow stream of air, and constituting a bifilar anemometer of the directional type. It was remarked [‡] that the disposition of the wires could be such that the temperature of the second wire of the pair was unaffected by the stream. In the course of an investigation of the velocity of the air-stream at successive cross sections in a flow tube, employing the hot-wire anemometer, the importance of this consideration became very evident, and the present communication details some of the characteristics of the forced convection of heat from a fine heated wire due to the passage of a stream of air moving with low velocity and heated by prior passage over a similar wire immersed in the stream. The dependence of this thermal effect upon the distance apart of the wires is, more especially, the subject of the present communication.

[*] Communicated by the Author.

[†] Phil. Mag. vol. xl. pp. 640-665 (1920).

[‡] *Ibid.* p. 652.

Experimental.

Details of the mode of insertion of the heated wires in the flow tube are given in fig. 1. The flow tube was made in two halves. The wires A were of pure platinum supplied by Messrs. Johnson & Matthey, and their length was as nearly as possible equal to the diameter of the flow tube. They were attached to pairs of copper leads B, B of 0·8 mm. diameter as previously described. The following device was finally adopted as the most suitable for maintaining the wires taut during the course of the experiments. The straight copper leads passed through holes affording a nice sliding fit in blocks of ebonite C fixed to the flow tube as shown. One pair of leads passed in similar manner through holes whose respective contours were about three-quarters of the circumference of a circle drilled at the edge of brass pieces D carried by supports G, H attached to the ebonite blocks C as shown. Similar holes through which the individual leads passed were provided in the brass pieces D_1 and D_2, and these leads were securely clamped by means of the screws E, the brass pieces being slotted for this purpose. The wires were maintained taut by means of the weak springs F pressing against the brass supports D_2, which slid freely along the surface of the supports G, H. The tension in the wires was adjusted by means of the screws J. In general, the variation of resistance of the wires due to tension was less than 0·1 per cent. of their resistance. The pair of leads shown in the upper part of the diagram was connected with screw terminals K by means of leads of loosely stranded copper wires. The distance apart of the heated wires could be adjusted to any desired value by the insertions of annular blocks L, accurately drilled to the diameter of the flow tube

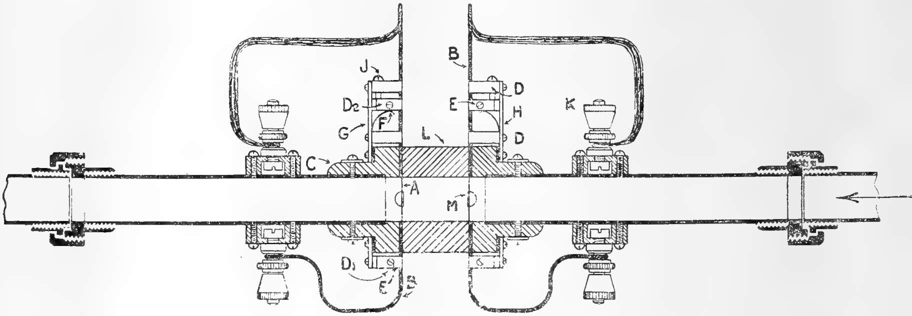


Fig. 1

between the ebonite blocks C. Care was taken that the continuity of the inner surface of the flow tube was nowhere disturbed by the insertion of the blocks, which were held rigidly in place against the blocks C by means of nuts screwing on the ends of three brass rods passing longitudinally through the whole length of the blocks. The distance apart of the wires was determined by means of a micrometer microscope reading direct to 0·001 cm. For this purpose, the wires could be viewed through the apertures M, which were normally closed by plugs whose ends conformed accurately with the inner contour of the flow tube. The tube was inserted in the flow system by means of spigot unions as shown. The wires were disposed in a horizontal plane in the flow tube, which was arranged horizontally. The distance apart of the wires having been ascertained, the current in the wires was adjusted by means of a rheostat, so that for the respective distances the wires were, in the absence of any impressed stream, maintained at a constant temperature, and subsequently the current in the flow experiments was adjusted to such appropriate value and maintained constant to within 0·001 amp. The experiments were directed mainly to ascertaining the change in resistance produced in the second wire of the pair by the stream of air, and for this purpose the ends of this wire were connected to a Rayleigh potentiometer, constituted of two P. O. boxes, in which the total resistance was throughout adjusted to 10,000 ohms. The working current in the potentiometer was derived from a Leclanché cell, and the readings were reduced to volts by calibration from time to time against a Weston cell certified by the N. P. Laboratory. The flow of dry air was established as detailed in previous papers, and the mean equivalent velocities of flow were throughout reduced by calculation to 0° C. and 760 mm. pressure.

Results and Discussion.

Internal Diameter of Flow Tube	2·011 cm.
External Diameter of Flow Tube	2·212 cm.
Mean Diameter of Platinum Wires	0·101 mm.
Temperature Coefficient of Platinum Wires	0·003750
R_0 of 1st Wire of Pair	0·2468 ohm.
R_0 of 2nd Wire of Pair	0·2420 ohm.
Resistance of 2nd Wire, heated in absence of impressed Stream	0·6931 ± ·0011 ohm.
Mean temperature of 2nd Wire, heated in absence of impressed Stream	531° C.

The pressure in the flow tube did not exceed 0·1 inch of water during the course of the experiments, and at this pressure it was ascertained that there was no appreciable leakage in the flow system.

In fig. 2 the changes of resistance of the second wire of the pair from its initial value in the absence of flow are plotted as ordinates against the values of the velocity of the impressed stream as abscissæ for various values of the distances apart of the wires. For the sake of clearness, only about one-quarter of the experimental points are indicated in the several curves. The calibration curve obtained when the second wire alone was heated is likewise shown in the diagram. For purposes of discussion the various curves are best grouped as indicated by the brackets in the table of distances apart of the wires given in the figure. Considering the first group corresponding to distances apart of the wires

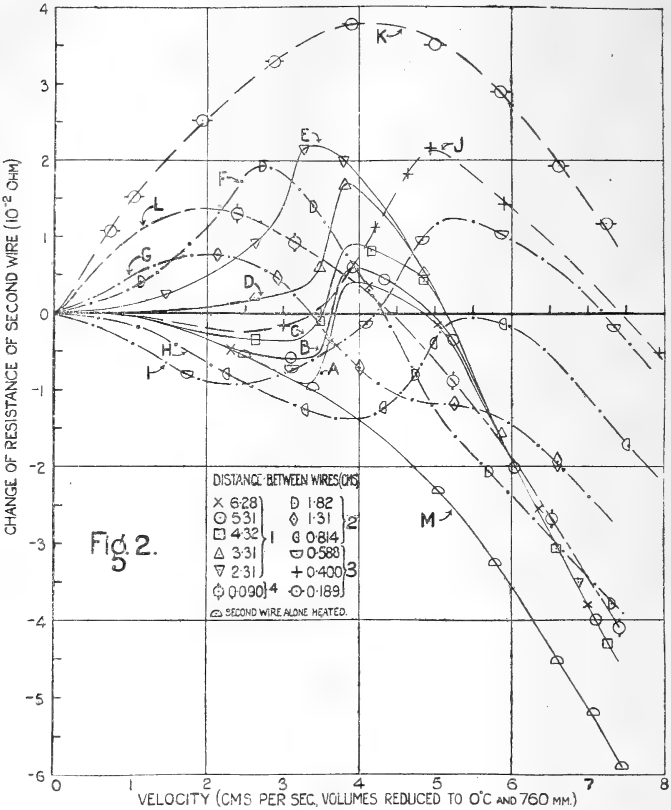


Fig. 2.

equal to 6·28 cm., 5·31 cm., 4·32 cm., 3·31 cm., and 2·31 cm., indicated by the curves A, B, C, D, and E respectively, it is seen that this group is characterized by a gradual increase in the maximum temperature attained by the second wire of the pair as the distance apart decreases. The initial portions of the curves A, B, and C approximate to the form of the initial portion of the curve L, obtained when the second wire alone was heated. Moreover, the initial cooling effect experienced by the second wire when the velocity of the impressed stream is small is reduced as the distance apart is diminished until it is replaced by an initial heating effect in the case of the curves D and E. This is in accordance with anticipations based on the consideration of the resultant thermal effect experienced by the second wire as being conditioned by two opposing tendencies, viz. the direct cooling effect due to the impressed stream, and heating effect arising from the forced convection of heat by the stream from the first to the second wire [*]. It will be noticed that corresponding to the higher values of the impressed velocity of the stream, portions of the curves A, B, C, D, and E are, within the limit of experimental error, common to the several members of this group. Moreover, as the distances apart of the wires become less, the value of the impressed velocity at which the respective curves unite is reduced. This result is readily deduced from a graphical consideration of the direction of the resultant stream due to free and forced convection from the wires as previously explained [†]. The second group of curves is constituted of curves E, F, G, and H, the curve E being included as affording a transition from the first to the second group. In this group, the maximum temperature attained by the second wire diminishes as the distance apart of the wires diminishes. The respective values of the maximum increase of resistance characteristic of the various curves are plotted and lettered appropriately to the respective curves in fig. 4, which is discussed later. It will be noticed that, as shown by the curve H, when the distance apart of the wires is 0·814 cm., for no value of the velocity of the impressed stream does the second wire become heated above its initial temperature. The characteristic feature of this group of curves arises owing to the respective distances apart of the wires in the cases in question being such that, in the absence of an impressed flow, the temperature of each wire is determined in part not only by the heated air accumulated in the upper portion of the cross

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[*] Proc. Phys. Soc. vol. xxxii. Part iii. p. 203 (1920).

[†] Phil. Mag. vol. xli. p. 247 (1921).

section of the tube and originating in the wire in question, but also in part by that similarly accumulated due to the other wire of the pair. This accumulation of a comparatively stagnant layer of heated air extending over a comparatively large distance in the upper region of the flow tube, is an additional factor complicating the application of the hot-wire anemometer to the investigation of the velocities (and more especially of low velocities) of gas streams in narrow channels. Thus, as shown by the initial portions of the curves H, I, and M, for small values of the impressed velocity, the second wire may be more cooled when the first wire is heated than when the wire is not heated. In the case of curves E–H, the initial value of the resistance of the second wire being determined while the wire is subjected to the heating effect just referred to, and as, moreover, this heating effect due to the accumulated layer of hot air clearly increases as the wires approach one another, it is to be anticipated that with the reduction or removal of this effect by the incidence of the impressed stream of air, the maximum increase of resistance of the second wire will be reduced as the distance apart of the wires is decreased. A further feature of the curves E to H (and the same may be said of all the remaining curves except L) is that, as the distance apart of the wires decreases, the resistance of the second wire corresponding to a definite *large* value of the impressed velocity of the stream increases. This arises owing to the diminished loss of heat occurring in the forced convection stream during the time of passage from one wire to the other as the distance apart of the wires is diminished. The third group of curves H, I, J, K is characterized by a gradual increase in the maximum temperature of the second wire as the distance apart of the wires diminishes. In the case of the curve K, corresponding to a distance apart of the wires equal to 0·189 cm., the maximum increase of resistance of the second wire occurring in the present series of experiments was attained. The degree of symmetry about a vertical axis through the apex shown by this curve indicates the elimination or compensation of the disturbing influences referred to above, and points to a disposition of the wires at a distance apart equal to about 0·2 cm. as most suitable for the construction of a bifilar or directional hot-wire anemometer. The gradual *increase* in the maximum temperature attained by the second wire as the distance apart of the wires is decreased, contrasted with the gradual decrease in the maximum in the case of the second group of curves (E–H) discussed above, is to be explained as follows:—

In the case of all dispositions of the wires, one contemplates the temperature of the accumulated hot layer of air, due to any one wire, as being greatest vertically above the wire, and diminishing right and left of the wire. Now, if the wires be considered as so widely separated that the accumulated layers due to the respective wires just overlap, it is clear that the effect of an impressed stream of low velocity would be to displace away from above the second wire the hot central portion of the one accumulated layer of *hot* air, and to bring up the comparatively *colder* border region of that due to the first wire. The net effect, on this account only, would be a considerable fall in the temperature of the second wire. If, however, the wires were so close together that considerable overlapping of the respective accumulated layers of hot air occurs, then any similar displacement of the central hot region of the accumulated hot strata above the second wire is accompanied by the convection thereto of the central hot region of the strata originating in the first wire. The consequent fall of temperature of the second wire is therefore less in this latter case than in the former. Considering the forced convection from the wires, it is readily seen that the net rise of temperature must therefore be greater in the latter than in the former case. The effect of the displacement of the comparatively stagnant accumulation of hot air above the wires therefore tends to be reduced as the wires approach one another, and consequently the temperature attained by the second wire due to an impressed stream of small velocity tends to be conditioned to an increasing degree by the convection of heat from the two wires alone.

The last group of curves is constituted of K and L. The curve L, like the curve K, possesses considerable symmetry. With closer approach of the wires to one another than that corresponding to K, the maximum increase of temperature of the second wire diminishes. That an effect of this nature must occur is clear from the consideration that when the distance apart of the wires is zero, *i. e.* the wires are coincident, no *heating* effect due to the impressed stream can be experienced by either wire, the calibration curve then assuming the form M. In the case of distances apart now being considered, these are so small, that due to an impressed stream the approach towards the second wire of the convection current arising from the first wire is likewise small. The consequent increase of temperature of the second wire due to such approach will therefore be small. Moreover, as the magnitude of the approach in question is proportional to the distance apart of the wires, the thermal effect on the second wire due to this cause will clearly diminish as the wires are brought closer together. Briefly it can be stated that with the closer approach of the wires at these distances, the temperature of the second wire becomes less dependent upon the inclination of the convection current from the first wire to the impressed stream.

As the matter referred to above is of some importance in the design of practical types of thermometeric hot-wire anemometers * for the measurement of the flow of gases in pipes, some further experiments were made with a view to ascertaining how the increase of temperature indicated by the second wire through which a current of 0·01 amp. only was maintained depended upon the distance of this thermometric wire from the heated wire in which a constant current equal to 1·3 amp. was maintained. The resistance of the thermometric wire was determined by means of a Callender & Griffiths bridge, and the bridge balance could be accurately adjusted to 0·1 mm. The results obtained are shown in fig. 3. To prevent confusion, a few only of the experimental points are given. An enlarged diagram of the form of the various curves in the neighbourhood of the origin is given in fig. 3 A, in which the effect of the accumulated strata of heated air to which reference has been made is clearly seen from the form of the curves F, G, H, and I. Although no actual cooling of the thermometric wire is shown by the curves B, D, E, the effect of the heated strata is not entirely absent, as is shown by the forms of the curves in the region of impressed velocities corresponding to 3–4 cm. per second. Certain features of the curves J, K, and L in fig. 2 are clearly reproduced in the corresponding curves J, K, and L in fig. 3. Attention may in particular be directed to the result that, as shown by the curves K and L, the effect of an impressed stream *moving with considerable velocity* may be to cool the thermometric wire below its temperature in the absence of flow and in the presence of the heated wire. The curves A′ and A″ correspond to greater distances of separation of the wires than any shown in fig. 2. Clearly, for all dispositions of the wires, an appropriate velocity of the impressed stream exists such that the temperature of the thermometric wire attains its maximum value due to an impressed stream of air passing in succession over the heated wire and the thermometric

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* See *e.g.* C. C. Thomas, Journ. Franklin Inst. 1911, pp. 411–460; Trans. American Soc. Mech. Eng. 1909, p. 655. See also Phil. Mag. vol. xli. p. 258.

wire. It will be observed that the value of the impressed velocity at which the respective maxima are attained becomes less as the distance between the wires diminishes. Below such value of the impressed velocity, the behaviour of the thermometer type of hot-wire anemometer is conditioned largely by the relative disposition of the wires both with regard to one another and to the walls of the channel in which the flow occurs. This point is of no little consequence in the technical application of this type of hot-wire anemometer, as the velocities occurring in gas mains are frequently below those to which reference has just been made. Further consideration of this matter is deferred, however, until the completion of an investigation at present in progress, using three platinum wire grids inserted in the flow tube, the central one functioning as a heating grid between two thermometric grids.

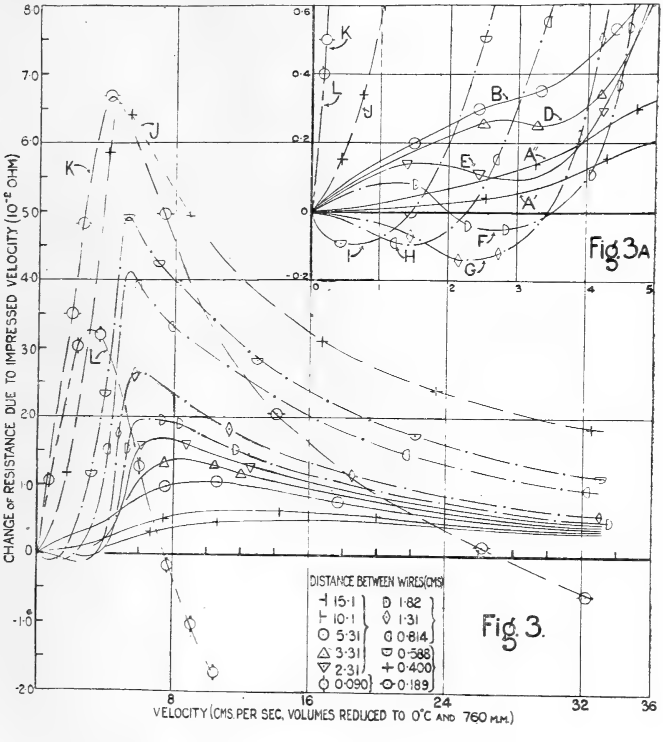

Fig. 3A

Fig. 3.

The values of the maximum increase of resistance of the second wire due to the impressed stream, derived from figs. 2

and 3, are plotted in fig. 4 as ordinates against the corresponding separation of the wires as abscissæ. In general, it is to be anticipated that such maxima will be less in the case when both wires are heated than when the first wire alone is heated, as in the latter case no appreciable cooling effect of the second wire as a direct convection effect due to the impressed stream is present to reduce the heating effect arising from convection of heat from the first wire to the second wire. The results shown are in agreement with this anticipation, except when the wires are separated by distances of from 2 to 4 cm. For such distances the maximum attained when both wires are heated is greater than the corresponding maximum when one wire alone is heated. In these cases, the distances apart of the wires are such that, owing to the impressed stream, the resultant convection from the first wire results in the region about the second wire becoming heated above that ruling in the absence of flow; thereby the velocity of the free convection current arising from the second wire

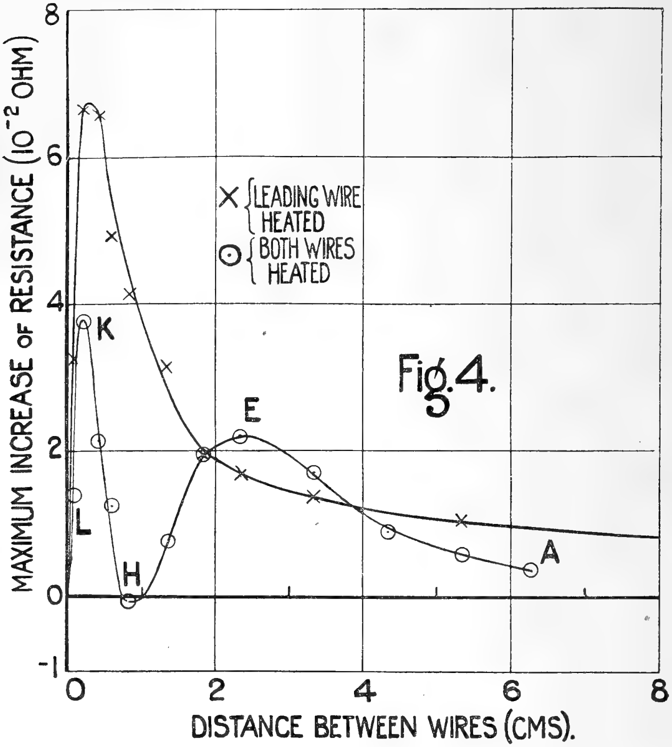

Fig. 4.

is reduced, with consequent rise of temperature of the second wire. Such an effect would be absent when the second wire conveys only a very small current. From what has been already said, it is clear that the distances of the wires apart involved in this consideration are somewhat greater than those considered in the discussion of the curves E to H (pp. 281–2).

The experimental work detailed herein was carried out in the Physical Laboratory of the South Metropolitan Gas Company, and the author desires to express his gratitude to Dr. Charles Carpenter, C.B.E., M.I.C.E., for the provision of the facilities necessary for the prosecution of the work.

Physical Laboratory,
South Metropolitan Gas Co.,
709 Old Kent Road, S.E.
Aug. 15, 1921.

XXVIII. *Observations and Experiments on the Occurrence of Spark Lines (Enhanced Lines) in the Arc.*—Part I. *Lead and Tin.*

By G. A. Hemsalech *and* A. de Gramont *.

[Plates III.-V.]

Contents.

§ 1. *Introduction.*

In the course of his classical series of laboratory experiments Sir Norman Lockyer observed that certain spectrum lines which were absent from the flame and relatively feeble in the arc, became bright relative to other lines when a powerful condenser spark was used as the source of light. The name "enhanced lines" was given to this particular type of light radiations, and their relative strengthening on passing from the flame to the arc and

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* Communicated by the Authors.

spark was attributed to increase of temperature. It appears, however, that Sir Norman Lockyer originally used the term "temperature" to include the possible effects of electrical variations*. This fact seems to have been forgotten subsequently, for the word temperature has since been used solely in its strictly thermal sense both by astronomers and spectroscopists, with the result that the enhanced lines (also called spark lines or high temperature lines) play now a prominent rôle in the temperature classification of the stars. One such enhanced line—namely λ4481 of magnesium—has even been strongly recommended for use as a stellar thermometer.

The first note of warning against the assumption that changes of temperature are responsible for the emission of enhanced lines seems to have been struck by Messrs. Liveing and Dewar †, who observed the spark lines of magnesium in an arc passing between thick rods of the metal in air, nitrogen, hydrogen, and other gases. The conclusions arrived at by these spectroscopists are best restated in their own words: "Our observations, however, render doubtful the correctness of the received opinion that the temperature of the spark discharge is much higher than that of the arc" . . . . . "Heat, however, is not the only form of energy which may give rise to vibrations, and it is probable that the energy of the electric discharge as well as that due to chemical change, may directly impart to the matter affected vibrations which are more intense than the temperature alone would produce."

The appearance of spark lines in the arc in the presence of hydrogen was again observed by Professor Crew ‡ and by Messrs. Fowler and Payne §. Messrs. Hartmann and Eberhard, who obtained spark lines in an arc burning under water, attributed their emission under these conditions to the hydrogen released by electrolysis around the electrode ‖. In a further series of experiments Hartmann varied the current strength in an arc passing between magnesium poles in air, and obtained the astonishing result that the enhanced line λ 4481 becomes the stronger as the current strength is lessened ¶. Similarly he obtained the spark lines of Zn, Bi, and Pb, which do not show in the carbon arc, in an arc

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* Nature, vol. lxxi. p. 400 (1905).

† Liveing and Dewar, Proceed. Roy. Soc. vol. xliv. pp. 241–2 (1888).

‡ Henry Crew, Astrophysical Journal, vol. xii. p. 167 (1900).

§ Fowler and Payne, Proceed. Roy. Soc. vol. lxxii. p. 253 (1903).

‖ Hartmann and Eberhard, Astrophysical Journal, vol. xvii. p. 229 (1903).

¶ Hartmann, Astrophysical Journal, vol. xvii. p. 270 (1903).

passing between metal poles using a feeble current with small vapour production. If, on the contrary, the amount of vapour was increased by heating one of the poles, the spark lines would disappear. As a general result of all his observations Professor Hartmann arrives at the conclusion that the spark lines do not correspond to a thermal radiation, but rather to electro-luminescence.

By carefully exploring the various regions of electric arcs burning steadily between metal electrodes, Messrs. Fabry and Buisson * and Professor Duffield † independently discovered the emission of spark lines in the immediate vicinity of the poles. Messrs. Fabry and Buisson attribute the emission of spark lines under these conditions to the high drop of potential which exists near the poles. According to their view the ions would attain very high speeds near the poles, and their collisions would give rise to the emission of light radiations which could not be produced with low velocity ions. Temperature would in this case not intervene at all. On the other hand, temperature by itself, if sufficiently high, might give similar ionic velocities in the absence of all electric actions.

But spark lines have been observed also in flames under certain conditions. Thus Messrs. Hemsalech and de Watteville have shown that certain enhanced lines of iron are emitted by the inner cone of the air-coal gas flame ‡. As most of these lines were not seen in high temperature flames, it seemed most plausible to connect their appearance in the air-coal gas cone with the special chemical actions prevailing therein. In discussing these results one of us directed attention to the existence of several different types of enhanced lines and, in a communication to the International Union for Cooperation in Solar Research, proposed the following provisional classification of enhanced lines §:—

1*st type*.—Lines which are enhanced on passing from flames of low to those of high temperature. Examples : λ 3934 and λ 3968 of calcium.

2*nd type*.—Lines emitted by the inner blue cone of the air-coal gas flame but absent from the mantles of the hotter flames. Only traces of a few of them have been observed in the hottest region of the oxy-acetylene flame.

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* Fabry and Buisson, *Journal de Physique*, vol. ix. p. 929 (1910).

† G. W. Duffield, Astrophysical Journal, vol. xxvii. p. 260 (1908).

‡ Hemsalech and de Watteville, *Comptes Rendus de l'Académie des Sciences*, t. cxlvi. p. 1389 (1908).

§ Hemsalech, Transactions Int. Union Solar Research, vol. iv. p. 145 (1914).

In the arc they are generally confined to the neighbourhood of the poles. Examples: the iron lines λλ 3872 and 3936, and a number of "polar lines" observed by Professor Duffield.

3rd type.—These lines are absent from flames and from the tube furnace. In the arc they appear as relatively feeble lines but are appreciably enhanced in the spark. Examples: the iron lines λλ 4924 and 5018, and the cadmium line λ 4416.

4th type.—The characteristic spark lines. Examples: λ 4481 of magnesium and λλ 4912 and 4924 of zinc.

More recently one of us observed that certain spark lines which are absent from an arc passing between a carbon rod and a metal electrode would show up well when the arc is taken between two big pieces of metal[*]. Further, with the aid of visual observations of the spectrum he noticed that whilst certain spark lines remained visible throughout the duration of the arc and could thus be photographed along with the arc lines, others flashed up only momentarily at the beginning when the arc is struck. He thus established the existence of two types of spark lines emitted by the arc, namely:

1. Lines which are permanently emitted.
2. Lines which appear only momentarily at the anode on striking the arc.

Experiments made with plate furnaces raised to over 3000° C.—thus approaching the temperature of an arc but in which the acting electric fields were relatively feeble—had failed to reveal the least traces of spark lines in the case of magnesium[†]. It was therefore thought that possibly a high degree of ionization, such as obtains in an electric furnace, would prevent the excitation of spark lines by opposing the establishment of high potential gradients. For it seemed to us that the electrical conductivity of the metal vapours at the moment of striking the arc, as also of those in an arc which passes between voluminous lumps of metal possessing a big thermal capacity and a large cooling surface, would be appreciably lower than that of the well protected vapours in a high temperature furnace. Stimulated by these considerations we decided to make a series of experiments with the object of ascertaining the relative rôles played by thermal, chemical, and electric actions in the emission of spark lines by an electric arc. Accordingly, our observations bear more specially upon the effect of cooling

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[*] A. de Gramont, *Comptes Rendus de l'Académie des Sciences,* clxx. p. 31 (1920).

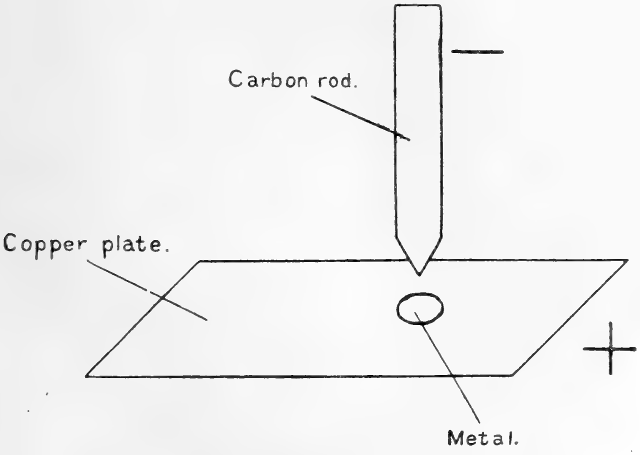
[†] Hemsalech, Philosophical Magazine, vol. xl. p. 308 (1920).

and heating the arc vapours or the electrodes, and upon that of varying the nature of the medium in which the arc is established. The present paper deals more particularly with the arc spectra of lead and tin.

§ 2. *A convenient arrangement for obtaining the arc spectra of metals having low melting-points.*

The usual way of obtaining the arc spectrum of a metal is to place small lumps of it into the hollowed out positive crater of the lower carbon rod. The inconveniences attending this method are well known; the temperature of the crater is so high that metals of low boiling-point are almost immediately thrust out again. The remedy generally applied is to use some compound of the element in place of the metal. It is obviously impossible under these conditions to carefully examine the spectrum radiations emitted by the vapour in the immediate vicinity of the metal, and it is probably for this reason that the emission of spark lines by the arc has passed unnoticed for so long. For the purpose of the present research it was essential to be able to explore the region around the metal from which the arc was made to pass, and the following simple method was found to fulfil these requirements. The piece of metal is laid upon a plate of copper about 5 by 10 cm. in area and not less than one millimetre thick. This plate remains fixed in position and is connected to the positive conductor of the electric supply circuit (fig. 1). A pointed carbon rod, which can be

Fig. 1.



Method ot obtaining arc spectra of volatile metals.

raised and lowered by means of some mechanical device, is placed vertically above the lump of metal and communicates with the negative end of the circuit. The arc is started by lowering the carbon rod and bringing it into contact with the piece of metal. As soon as the arc is struck the metal melts and forms a globular mass from which the arc continues to burn quite steadily. The rôle of the copper plate is, naturally, to dissipate the heat generated by the arcing, and thus to prevent the rapid boiling away of the metal. With this device good continuous arcs have been obtained with the following metals: Sb, Bi, Mn, Na, Sn, Cd, Zn, Pb, Tl, Al, Mg, and Li.

§ 3. *Spectroscopic methods employed.*

Nearly all our observations were made photographically. In order to cover the whole region of the spectrum between λ 2150 and λ 7000 the following three instruments were made use of:

1. Quartz spectrograph provided with one 60° Cornu-prism for the region from λ 2150 to λ 3200.
2. Uviol glass spectrograph by Hilger with two 60° prisms for the region λ 3170 to λ 5000.
3. Glass spectrograph covering the region λ 3600 to λ 7000 and consisting of three 45° prisms by Steinheil.

Lockyer's method of projecting an image of the source upon the slit was used throughout, and the focussing and adjustment of the electrodes upon the slit were done in the manner previously described by one of us [*].

§ 4. *Preliminary observations.*

An arc was established between metallic lead and a carbon cathode with the arrangement described in §2. Both visual and photographic observations failed to reveal any trace of spark lines even in the immediate vicinity of the molten metal. During these experiments our attention was attracted by the strong heating of the carbon cathode, the tip of which became white hot almost from the moment of starting the arc. We concluded from this observation that large numbers of the electrons expelled by the incandescent carbon were shot through the arc gap and, by reason of their intense ionizing action, were lowering the resistance of the medium through which the arc was passing. Accordingly, in a

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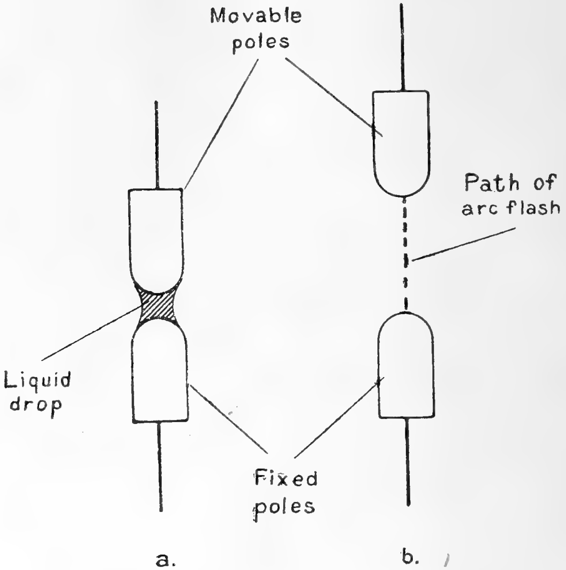
[*] Hemsalech, Philosophical Magazine, vol. xl. p. 316 (1920).

subsequent experiment the carbon was replaced by a rod of graphite. Under otherwise similar conditions as before, the tip of the graphite cathode did not become white hot during arcing and, perhaps as a consequence of this deficiency, the arc burned most unsteadily and was difficult to keep going for any length of time. We concluded that, since evidently fewer electrons were being expelled from the graphite than from the white-hot carbon, the resistance of the medium through which the arcing current passed was greater in the case of the graphite arc than in that of the carbon arc. Consequently, it would necessitate the application of a stronger electric field in order to drive the electric current through a graphite arc and to maintain the latter stable. Now, with a graphite cathode the spark lines of lead became visible in the arc! This result seemed to us to mean that an increase of the resistance of the medium, or otherwise stated a lowering of the degree of ionization prevailing therein, is one of the conditions for the appearance of spark lines in the arc. In order to test this inference the carbon cathode, which in the first experiment had prevented the emission of enhanced lines, was again mounted in the apparatus, and the resistance of the medium between the carbon tip and the lead anode increased by gently blowing through it with the mouth. This very simple *modus operandi* produced the looked for effect, for the spark lines of lead were brought out quite plainly!

§ 5. *Effect of a drop of liquid placed between the electrodes.*

Previous experimenters had obtained the spark lines in the arc by burning the latter under water; but, unless the liquid be constantly renewed, it soon becomes opaque with colloidal matter, and detailed observations are thereby seriously impeded. We therefore looked for some more convenient method of attaining the same object, and finally adopted the following very simple process of changing the nature of the medium through which the arc was passed, at all events during the early stages of the discharge. The two electrodes, one of which may be a carbon or graphite rod, are so arranged that the lower one (generally the metal and either positive or negative) remains fixed, whereas the upper one can be rapidly moved up and down by means of a vertical rack motion. Both are well rounded off at the ends and present a smooth surface. After the current has been put on the electrodes are first brought to within about two or three millimetres from one another, and by means of a small camel's hair brush a drop of some transparent liquid, such as distilled water, paraffin oil, glycerine, turpentine, alcohol, etc., is placed in the small gap between them, where it is held in position by capillary forces (fig. 2 *a*). The electrodes are now brought into contact, and then separated again by swiftly raising the upper electrode to a distance of several centimetres from the stationary one so as to avoid the establishment of a stable arc (fig. 2 *b*). We estimate that in our experiments the velocity of the electrode as it moves upwards is at least one metre per second, so that the luminous phenomena observed along the path of the arc follow each other in rapid succession. The relative position of any luminous effect along the gap will therefore provide us with an indication as to which part of the discharge it corresponds.

Fig. 2.



Method of producing arc in liquid media.

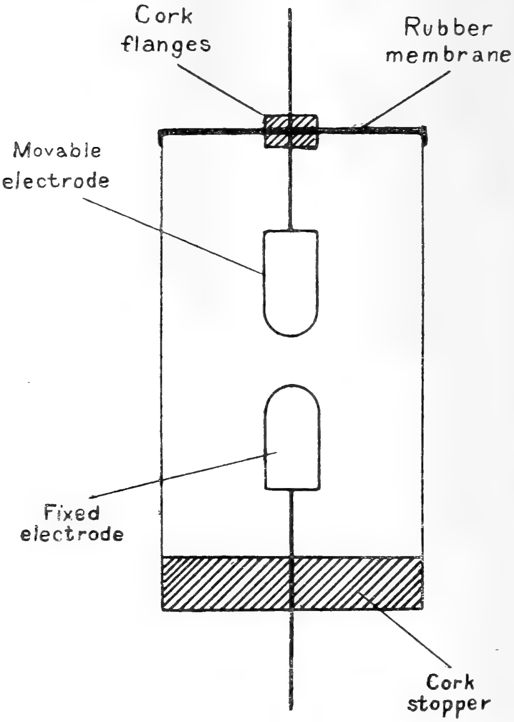
The luminous phenomenon obtained in the way described is composed of two distinct phases. At the instant the electrodes separate a discharge begins to pass between them through the thin liquid film. When the distance between the electrodes has grown to from about 0·1 to 0·5 millimetre, varying according to the nature of the liquid, the *first phase* of the phenomenon comes to an end with the destruction of the liquid film. It is during this phase—namely, within the liquid film—that the spark lines are brought out and attain a relative development comparable to that observed in condenser discharges. After the destruction of the film a short-lived arc flash is formed between the fixed and the upward moving electrode, resulting in the establishment of the *second phase.* During this phase both flame and arc lines are well developed, whereas the spark lines show only feebly, and sometimes stop quite abruptly in the middle of the arc flash, as though some sudden change in the structure of the radiating centre had taken place. According to our estimates the first phase during which the spark lines are strongly emitted lasts from about 0·0001 to 0·0005 second; the second phase may last up to 0·007 second or even longer. The description of the observed phenomena just given applies to various kinds of liquid films, both insulators and conductors. When the liquid is an electrolyte the electrodes need not be metals. Thus the spark line λ 4481 of magnesium is brought out in a film of magnesium sulphate solution placed between graphite electrodes. In addition to the spectrum of the metal vapour the hydrogen lines λ 4862 and λ 6563 are emitted with all these liquids. Their behaviour is very significant—namely, they are considerably broadened at the beginning of the first phase and grow narrower as the distance between the electrodes increases.

§ 6. *Effects of various gases.*

Since our principal object was to ascertain more precisely at which stage of development of the arc phenomenon various types of lines are emitted, it was essential to draw the arc out by rapidly displacing one of the electrodes in the manner described in the preceding paragraph. In order to accomplish this in a small enclosed space filled with the gas under examination the following method was employed (fig. 3). A cylindrical glass vessel of two inches diameter and five inches height was closed at the bottom with a stopper which carried the fixed electrode. The top of the glass vessel was covered with an elastic rubber membrane through which passed the movable pole. The latter could be brought into contact with and withdrawn vertically from the fixed electrode by means of a mechanical device. The gases employed—namely, hydrogen, nitrogen, oxygen, and coal gas—were passed through this vessel in a constant stream at a little more than atmospheric pressure.

Without entering into details it will suffice here to state that practically in every case the spark lines were brought out strongest during the early stages of the arc when the distance between the electrodes was still very small. Both hydrogen and coal gas gave them more prominently than the other gases. The red and blue lines of hydrogen (H_α and H_β) were brought out along with the spark lines when the arc flash was taken in the first named two gases, and a significant feature of all these lines is their remarkable broadening, especially during the very early stages of the discharge. In this respect they resemble their appearance in condenser discharges. Although the spark lines are likewise brought out in oxygen, they are not so prominent relatively to the arc lines as in hydrogen. In nitrogen the spark lines of lead are fairly marked at the initial stage, but those of magnesium show only feebly. With the last

Fig. 3.



Method of obtaining arc in gases.

named metal as electrodes in this gas a stable arc becomes established. This fact of course implies a state of high conductivity of the vapours—a condition which, as our previous results had shown, is adverse to the emission of spark lines.

§ 7. *Arc in liquid air.*

Our preliminary experiments had taught us that spark lines are brought out when the electrodes, especially the cathode, remain relatively cool during arcing, as for example when a graphite rod is used facing a metal pole. It seemed therefore desirable to make some observations on the spectrum of the arc with the electrodes cooled down to the temperature of liquid air—namely, to about −190° C. It was obviously not possible to apply the method of the liquid drop to this case ; therefore the electrodes were mounted inside a double-walled, glass vessel and completely immersed in liquid air. No stable arc was obtained ; only short arc flashes, each one of which was accompanied by the evolution of numerous air bubbles caused by the boiling of the liquid around the path of the discharge. In the spectrum of these luminous flashes the spark lines or so-called high temperature lines were strongly developed, and generally remained visible till the end of the flash. The flame lines, on the other hand, were relatively feeble. The arc lines showed a normal development as in an ordinary arc. Besides confirming our previous conclusions with regard to the effect of cooling of the vapour on the appearance of the spark lines in the arc, these results further emphasize the fact that the presence of hydrogen is not essential for their emission.

§ 8. *Nomenclature employed in this research.*

In connexion with the various modes of obtaining the arc spectra of metal vapours as detailed in §§ 2–7, the following denominations will henceforth be adopted in order to secure precision and avoid repeated explanations.

1. *Carbon or graphite arc.*—Arc formed between a metal and a carbon or graphite rod.
2. *Direct arc.**—Arc passing between two metal electrodes.
3. *Ordinary arc.*—A carbon, graphite, or direct arc burning steadily and continuously. Observations, either visual or photographic, are begun only *after* the arc has been started and are stopped *before* the arc is extinguished.

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* A. de Gramont, *loc. cit.*

4. *Blown arc.*—Air is blown through the arc, either with the mouth or otherwise, from the moment of striking it until its extinction.
5. *Water arc, glycerine arc, etc.*—Arcs through liquid films according to nature of liquid employed.

§ 9. *Results of observations.*

For taking the spectrographic records the image of the arc was so adjusted on the slit as to allow of perfect differentiation between the luminous radiations emitted at various stages of the phenomenon. For this purpose the images of the pole tips were made to coincide with the slit in such a manner that the motion of the image corresponding to the tip of the upper pole took place along the slit. Spectrograms obtained in this way permit of distinguishing at a glance between the radiations emitted by the discharge through the liquid film and those given out a little later during the arcing stage. Since a single arc flash did not always suffice to adequately impress the photographic plate a number of flashes, generally from 7 to 30, were given in succession ; a fresh drop of liquid was placed in position between the electrodes before each flash. It was found that the images of successive flashes were fairly accurately superposed upon each other. This was indicated by the sharply defined borders of the narrow spectrum near the stationary pole corresponding to the liquid film phase. In fact the definition of the spectra obtained in this way was generally such as to admit of the measurement both of the thickness of the liquid film and of the total length of the arc flash.

The electric current used for producing the arc was derived partly from a public supply service at 110 volts (Paris) and partly from a battery of accumulators at 80 volts (Manchester). The current strength varied generally between 5 and 10 amperes.

On account of the important rôle played by enhanced lines in astrophysical problems, special care was given to the investigation of that region of the spectrum which is most generally used by astronomers—namely, the region between λ 3600 and λ 7000 ; and it is mainly also for this reason that in addition to an estimation of the relative intensities of the lines their characters in either phase have been carefully noted. In order to facilitate the tabulation of these results the following numbers and signs have been made use of for expressing relative intensities and characters.

a. *Relative intensities of lines* :—

Feeble lines : ½, 0, 00, and 000, this last one being at the limit of perception.
Lines of moderate strength : 1 to 5.
Strong lines : 6 to 10.
Extra strong lines : 12 to 50.

b. *Character of lines* :—

—— = no line has been observed.
c = a long line, one which passes practically unaffected from one electrode to the other through the first and second phases.
d = a discontinuous line ; one which is emitted during the first phase and falls off rapidly or abruptly at the beginning of the second phase and disappears (abruptly or gradually) before the end of the second phase.
dd = a short line ; observed only during the first phase.
s = sharp.
n = nebulous and ill-defined.
} A line which is not specially marked s or n is tolerably well defined.
nn = broad and hazy.
b^r = winged or broadened towards red.
b^v = ,, ,, ,, violet.
b^{rv} = symmetrically winged or broadened.
r = reversed.
I = first phase.
II = second phase.
enh = enhanced line.

These signs are placed behind the numbers indicating the relative intensities of the lines.

I. *Arc spectra of Lead.*

a. Quartz spectrograph λ 2150 to λ 3200. Spark lines which are absent from the ordinary carbon-metal arc, but are brought out with a drop of water placed between the electrodes :—

λλ 2204	Very feeble in direct arc, but strong in water arc and spark.
2698	Well seen.
2950	Strong.
3018	Strong.

b. Uviol spectrograph λ 3170 to 5000.

λλ 3221
3240
3263 } Characteristic arc lines which disappear in water arc.
4341
4603
3787 Spark line; absent from carbon arc, feeble in direct arc and appreciably enhanced in water arc.

c. Reversals.

λλ 2237 Reversed in water arc, but not in direct arc or spark.
2247
2394 } Reversed both in direct arc and water arc; not reversed in spark.
2614
2833

d. Glass spectrograph λ 3600–λ7000.

Wave-lengths in I. A.	Ordinary arc in air between Carbon cathode and Lead anode.	Arc between Lead poles in				
		Nitrogen.	Oxygen.	Coal gas.	Liquid air.	
3683·5	10 crb^{rv}	10 crb^{rv}	4 cr	3 cr	5 cr	
3740·0	10 c	10 c	6 c,r at poles	5 cb^{rv}	8 cs	
3786·3	——	——	——	00 dd nn	——	enh.
4019·6	10 c	8 c	10 c	10 c	10 cs	
4057·8	20 crb^{rv}	25 crb^{rv}	30 crb^{rv}	50 crb^{rv}	30 crb^{rv}	
4062·2	4 c	5 c	4 c	8 c	5 cs	
4168·0	8 c	6 cs	8 c	7 c	8 cs	
4242·6	——	0 dd nn	$\frac{1}{2}$ dn	2 dn	00 dd n	enh.
4245·2	——	2 nn in I 1 n in II	4d, b^{rv} in I	15 b^{rv} in I 10 in II	5 in I 1 in II	enh.
4340·6	4 c	2 cn	0 cn	$\frac{1}{2}$ cn	2 c	
4386·9	——	2 nn in I $\frac{1}{2}$ n in II	5 b^{rv} in I 3 in II	15 b^{rv} in I 10 in II	5 d	enh.
5005·4	12 c	8 c	8 cs	8 c	8 cs	
5043·0	——	0 dd nn	0 dd nn	2 n b^{rv} in I 0 nb^{rv} in II	000 dd	enh.
5201·4	10 c	5 c	4 cs	3 c	4 cs	
5372·5	——	2 nn in I 00 n in II	3 in I 0 in II	10 b^{rv} in I 1 in II	1 dd	enh.
5544·8	——	1 nn in I 000n in II	2 n in I 00 n in II	3 b^{rv} in I $\frac{1}{2}$ in II	$\frac{1}{2}$ dd n	enh.
5608·9	——	10 in I 3 in II	10 in I 5 in II	15 b^{rv} in I 1 in II	6 in I 2 in II	enh.
5876·4	——	——	——	$\frac{1}{2}$ dd nn	——	enh.
6002·0	4 c	6 c	4 cn	3 cb^{r}	5 cs	
6011	2 c	2 cn	2 cnb^{r}	——	2 cn	
6059·9	2 c	1 cn	0 cnb^{r}	00 c	$\frac{1}{2}$ c	
6109	$\frac{1}{2}$ c	00 c	000 cn	——	000 c	
6234	1 c	0 c	00 c	——	00 c	
6660·0	——	2 in I 00 in II	5 in I 1 in II	8 in I 1 in II	1 in I 000 in II	enh.

Wave-lengths in I. A.	*Ordinary arc* in air between Carbon cathode and Lead anode.	*Water arc* between Carbon cathode and Lead anode.	*Blown arc* between Graphite anode and Lead cathode.	
3683·5	10 crb^{rv}	5 cr, b^{rv} in I	5 cr, b^{rv} in I	
3740·0	10 c	5 b^{rv} in I 3 in II	6 c	
4019·6	10 c	10 in I 4 in II	10 c	
4057·8	20 crb^{rv}	30 cr, b^{rv} in I	30 cr, b^{rv} in I	
4062·2	4 c	4 c	5 c	
4168·0	8 c	8 in I 4 in II	8 c	
4242·6	——	0 in I 000 in II	1 dd n	enh.
4245·2	——	8 in I 3 in II	6 in I 1 in II	enh.
4340·6	4 c	00 cnn	2 cn	
4386·9	——	8 in I 3 in II	6 in I ½ in II	enh.
5005·4	12 c	8 in I 4 in II	8 c	
5043·0	——	2 nn in I 000 in II	1 dd nn	enh.
5201·4	10 c	5 in I 2 in II	4 c	
5372·5	——	3 dd n	2 dd n	enh.
5544·8	——	1½ dd n	1 dd n	enh.
5608·9	——	8 d	8 dn	enh.
5876·4	——	00 dd	——	enh.
6002·0	4 c	½ cb^{r}	4 c	
6011	2 c	——	1½ cn	
6059·9	2 c	0 cn	1 cn	
6109	½ c	——	0 cn	
6234	1 c	——	½ cn	
6660·0	——	4 d	4 dd n	enh.
6790	——	½ dd	00 dd	enh.

II. *Arc spectra of Tin.*

a. Quartz spectrograph.

λλ 2531	Strong in direct arc	practically absent from water arc.
2558	,, ,, ,, ,,	
2632	Fairly strong in direct arc	
3284	Absent from direct arc	very strong in water arc.
3352	,, ,, ,, ,,	
4586	,, ,, ,, ,, ;	well marked in water arc.

b. Reversals.

The following lines are distinctly reversed in the direct arc but not in the water arc nor in spark: λλ 2200, 2210, 2246, 2269, 2287, 2317, 2335, 2355, 2422, 2430, 2707 and

2840. The line λ 2484 is only very feebly reversed in the direct arc and, like the other lines, not reversed in water arc and spark.

c. Glass spectrograph.

Wave-lengths in I. A.	Ordinary arc between Graphite anode and Tin cathode.	Water arc between Graphite anode and Tin cathode. 1st phase only.	
3801·0	15 cs	10 b^{rv}	
3907·2	——	000 n	enh.
4330·1	——	00 n	enh.
4524·7	10 cs	10 s	
4585·6	——	1	enh.
4618·2	½ dd	3	enh.
5100·4	——	000	enh.
5224·5	——	000	enh.
5332·6	1 dd n	10 n	enh.
5562·5	2 dd n	15	enh.
5589·0	2 dd n	10	enh.
5631·7	8 cs	2	
5799·2	2 dd	15	enh.
6149·6	6 cs	0 n	
6452·8	5 dd	20	enh.
6760	——	1	enh.
6844·3	1 dd	4	enh.

§ 10. *Explanation of Plates.*

The reproductions are made from enlargements of the original negatives. Plate III. gives portions of the ultra-violet regions of the spectra of Pb and Sn. *a* was obtained by photographing in juxtaposition on the same plate the spectra of the ordinary arc, water arc, and capacity spark between Pb electrodes. The spark lines λ 2950 and λ 3018, which are absent from the ordinary arc, are brought out in the water arc. Noteworthy is the strong reversal of λ 2833 in the water arc; this line is reversed only feebly in the ordinary arc and not at all in the spark. Photograph *b* shows the spectra of the ordinary and water arcs of tin (metal electrodes). The most remarkable feature is the prominence in the water arc spectrum of the two spark lines λ 3283 and λ 3352, which are absent from the spectrum of the ordinary arc.

On Plate IV. are reproduced portions of the visible region of the spectra of lead. *a*, *b*, and *c* were obtained with a carbon cathode (top) and Pb anode. *a* is the spectrum of the ordinary arc in air, showing the usual development under these conditions. The narrow strip of continuous spectrum along the upper edge is caused by the white-hot tip of the carbon cathode. There are no traces of spark lines in this spectrum. *b* was obtained with the same electrodes as *a*, but a current of air was blown through the arc from the moment of striking the same. The strip of continuous spectrum seen near the anode is produced during the first phase of the discharge; it is also at this stage that the spark lines λ 4245 and λ 4387 are most strongly developed. Arc as well as spark lines appear symmetrically widened or winged in the first phase. During the second phase the spark lines are relatively feeble, but they remain visible till the end of the arcing; air is of course passing through the arc all the time and keeps its ionization at a low value. Spectrum *c* was obtained with a drop of distilled water placed between a carbon cathode (top) and a Pb anode. In the first phase the spark lines λ 4245 and λ 4387 are relatively stronger than the arc lines λ 4020 and λ 4168. During the second phase the spark lines die out sooner than either flame or arc lines. Noteworthy is also the relatively great reduction in intensity of the flame line λ 4058. The C band at λ 4216 shows faintly throughout the second phase on the original negative. Spectra *d* and *e* were obtained with Pb electrodes in oxygen and coal-gas respectively. In both spectra the spark lines are strongest at the beginning of the arc flash when the poles were still near together; but they are likewise, though less intensely, emitted throughout the second phase. In coal-gas they are particularly strong and are only surpassed in intensity by the flame line λ 4058.

Plate V. gives the red region of the arc spectra of tin as obtained under various conditions. Spectrum *a* is that of an ordinary arc between a carbon cathode (top) and an Sn anode; no trace of a spark line is to be seen. *b* is the spectrum of an ordiaary arc between a graphite anode (top) and an Sn cathode: a number of spark lines are revealed in the vicinity of the metal cathode. These lines are relatively strengthened in the blown graphite arc as shown in *c*. With the water arc the spectrum consists predominantly of spark lines (spectrum *d*). A feature of this spectrum is the great intensity of the hydrogen line λ 6563.

§ 11. *Summary of Results.*

1. A convenient method has been established of obtaining the arc spectra of volatile metals. § 2.
2. Experiments are described which seem to indicate that spark lines are brought out in the arc when the degree of ionization is lowered, as for example, by blowing air through the arc. § 4.
3. A very simple method has been developed of studying the effect of various liquid media on the character of the arc spectrum of a metal. This method consists in placing a drop of the liquid between the poles before striking the arc. § 5.
4. The spark lines or so-called high temperature lines disappear from the arc when the cathode is formed by white-hot carbon. They are brought out prominently, on the other hand, when the electrodes are cooled down to about −190° C. by immersion in liquid air. §§ 4 and 7.
5. A detailed account has been given of the results of our observations on the relative behaviour of different types of lead and tin lines in the arc under various discharge conditions. §§ 9 and 10.

§ 12. *Concluding Remarks.*

It has been shown in the course of this research that the simple process of placing a drop of liquid between the electrodes of an arc provides a very convenient method of obtaining the spectrum of a metal vapour in which the spark lines are prominent and easily recognized as such. In this respect the liquid film arc resembles a capacity spark which likewise brings into prominence lines of this type. But our new arc method presents a decided advantage over the employment of capacity-sparks inasmuch as no air lines are brought out with the exception of the not very obnoxious lines of hydrogen. As is well known, the spectrum of a capacity-spark is infested by hundreds of air lines, which in many cases render the observation of the metal lines very difficult, and although the introduction of self-induction into the discharge circuit suppresses all the air lines, it also similarly affects the spark lines. Thus it seems to us that by further developing the new arc method, an effective means should be obtained not only of exciting spark lines in metal vapours, but also of finding out more about their origin and meaning. From the results of our present experiments we may already safely derive the following fundamental facts :—

1. The presence of hydrogen is not essential for the excitation of spark lines.
2. Spark lines attain a high degree of development only in a medium which offers a comparatively high resistance to the flow of electricity.
3. When hydrogen is present in the medium, either in the free state or in combination, its spectrum resembles that which is only observed with high tension condenser discharges—namely, its lines are symmetrically broadened as though under the influence of a strong electric field (Stark effect).

With the help of these facts we will now attempt to derive some notion as to the conditions which underlie the emission of spark lines (4th type enhanced lines) both in spark and arc. As is well known this particular type of lines is most strongly developed in a powerful capacity-spark passing between cold metal electrodes in air at atmospheric pressure. If one or both electrodes are raised to a high temperature the discharge becomes less violent, and the spark lines are considerably reduced in relative intensity [*]. The heat given off by the electrodes raises the conductivity of the air-gap between them, and the condenser discharge takes place at a much lower potential gradient than through cool, and therefore less conducting air. Again, in the self-induction spark the whole of the condenser discharge current passes through air and metal vapour which have been ionized already by the initial discharge (pilot spark). The spark lines in this case are either absent or only feebly developed and confined to the immediate vicinity of the poles. Thus the results with spark discharges teach us that the spark lines are brought out when the discharge passes through a medium which to begin with is only feebly ionized, so that a high potential gradient is required in order to force the electric current through it. As for the arc, it has been shown in this paper that spark lines are not emitted in the carbon arc when the cathode electrode is white-hot. On the other hand, when a graphite pole is used which does not heat to the same extent, spark lines become visible near

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[*] C. C. Schenck, Astrophysical Journal, vol. xiv. p. 130 (1901).

the metal pole. Again, if air is blown through the conducting vapours of the arc and their resistance thereby increased, spark lines are brought out prominently even with a carbon cathode. But the emission of spark lines by the arc is strongest when the formation of a proper arc, and, therefore, a rapid ionization of the medium, is prevented or, at all events, retarded by means of a liquid which fills the arc-gap. The flashing up of spark lines at the moment of striking an arc between cool metal poles in air may be accounted for by the scarcity of conducting vapours at this early stage ; for as soon as conducting vapours are formed in abundance resulting in the establishment of a steady arc with rise in temperature and increase in electrical conductivity (partly, perhaps, as a result of chemical reactions between the metal vapour and the constituent gases of the surrounding atmosphere), the spark-lines either disappear from the spectrum or show only as traces in the vicinity of the poles. The greater prominence of the spark lines when the arc is taken in hydrogen, may be due perhaps to the relatively small amount of chemical reaction which takes place between the metal vapour and this gas. In short, the whole of our experimental evidence points to the fact that spark lines are emitted when electric currents are passed through media (vapours or gases) which possess a low degree of ionization. Since such a process involves the application of powerful electric forces giving rise to the establishment of high potential gradients in the medium concerned, we are finally led to conclude that *the emission of spark lines is connected with the existence of strong electric fields.* A simple consideration shows indeed that for small pole distances the electric field within the arc-gap can be very great even with a small potential difference. Thus, for a pole distance of 0·05 mm. the intensity of the electric field with an applied potential of 110 volts is equal to 22,000 $\frac{\text{volts}}{\text{cm.}}$. As we have shown in the course of this research spark lines are strongly emitted by the arc only whilst the distance between the electrodes is precisely very small.

Manchester and Paris,
May 1921.

XXIX. *The Dependence of the Intensity of the Fluorescence of Dyes upon the Wave-Length of the Exciting Light.* By S. I. VAVILOV, *Lecturer in Physics at the University of Moscow* *.

THE connexion between the energy of exciting light and the intensity of fluorescence can be expressed on the ground of a precisely established experimental law † as

$$\int_0^\infty f_{\lambda_f} \, . \, d_{\lambda_f} = \mathrm{F} = \kappa \, . \, \mathrm{I}_\lambda \, . \, \alpha_\lambda \, . \, \Delta\lambda, \quad . \quad . \quad . \quad . \quad (1)$$

where $f_{\lambda f}$ is the energy of fluorescence corresponding to the interval of wave-lengths of fluorescence $d\lambda_f$, F the integral energy of fluorescence, I_λ energy of exciting light, α_λ the part of the light absorbed by the fluorescent dye in a finite small interval $\Delta\lambda$. The coefficient

$$\kappa = \frac{\mathrm{F}}{\mathrm{I}_\lambda \, . \, \alpha_\lambda \, . \, \Delta\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

gives the energy of fluorescence per unit of absorbed energy; we shall call it "specific fluorescence." The value of κ is generally a complicated function of λ. The first stage of the problem which arises here is the dependence of κ upon λ within an isolated absorption-band. An attempt at an experimental solution of this problem was made by Nichols and Merritt ‡. These authors found that the specific fluorescence of Eosin and Resorufin increases towards long wave-lengths, for Resorufin by 2·7 times (at the change of wave-length of exciting light from 520 $\mu\mu$ to 600 $\mu\mu$) and by 1·63 times for Eosin (480 $\mu\mu$ to 560 $\mu\mu$). The authors have stated a generalization of these results § without giving a theoretical explanation.

We suppose that the question of the dependence of κ upon wave-length inside an isolated absorption-band is closely related to the problem of the nature of these bands in liquid and solid bodies, and has equally considerable significance for the theory of dispersion and absorption as well as for its bearing upon the theory of fluorescence.

The fundamental law (1) shows the secondary character of fluorescence, which is regulated by the value of the energy accumulated in the given molecular resonator. In

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* Communicated by the Author.

† *Cf.* J. Hattwich, *Wiener Ber.* Bd. 122. Abt. 11 *a* (November 1913).

‡ E. L. Nichols and E. Merritt, Phys. Rev. I. xxxi. pp. 376, 381 (1910).

§ E. Merritt, Phys. Rev. II. v. p. 328 (1915).

the most probable supposition that such secondary processes as fluorescence and photochemical effect are conditioned exclusively by the intrinsic energy of the resonator and its constant mechanism, the value of κ must be constant for the whole region of absorption: *i. e.*, for a physically simple absorption-band. Such a conclusion is maintained by the old resonance theory of fluorescence of Lommel [*] and the modern theories which consider this phenomenon as a tertiary process of lighting which accompanies this or that process of dissociation of molecules [†]. A somewhat different result is given by the theory of Einstein, which will be mentioned later on.

From our standpoint, the inconstancy of κ inside an absorption-band is an indication of its physical complexity. Such a band is a result of a superposition of several bands belonging to resonators of different types: *i. e.*, with a different κ.

The classical theory of dispersion and absorption in all its modifications is forced to apply broadly the sign Σ in the explanation of absorption- and dispersion-bands of liquid and solid bodies [‡], which allows us to introduce any number of new empirical constants. The liberty in this operation is practically unlimited. It is essential that none of the experimental curves can be considered from this standpoint as a physically simple one. In all these cases we can, therefore, expect a variability of κ. As a criterion can be used also another secondary process accompanying the absorption of light—the photochemical effect, as was shown by Lasareff [§]. Therefore the experimental result of Nichols and Merritt is an argument in favour of the classical theory of dispersion and absorption.

Another supposition about the nature of broad absorption-bands was proposed by Kravec [||] and qualitatively by Webster [¶]. Their supposition consists in that occasional influence of fields of surrounding moving molecules (or parts of the same molecule) can in some way modify the frequency of a resonator towards both sides. The molecules will be distributed along the frequencies following the law

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[*] E. Lommel, *Wied. Ann.* iii. p. 251, § 19 (1878).

[†] E. Merritt, *loc. cit.*

[‡] *Cf.* H. Kayser, *Handbuch der Spectroscopie*, Bd. iv. p. 457 ff. B. J. van der Plaats, *Ann. d. Phys.* xlvii. p. 429 (1915).

[§] P. Lasareff, *Ann. d. Phys.* xxiv. p. 661 (1907).

[||] T. R. Kravec, 'The Absorption of Light in Solutions of Dyes,' Moscow, 1912, p. 106.

[¶] D. L. Webster, Phys. Rev. II. iv. p. 177 (1914).

of probability. The experimental curve of absorption is therefore a probability curve, enclosing the family of theoretical curves with a variable parameter—its frequency. For an explanation of the experimental curves from the standpoint of this hypothesis it was unfortunately necessary to suppose at least two types of resonators. Therefore in this theory the absorption-band of dyes is also a complex one.

Many experimental facts and theoretical consequences necessitate a fundamental revision of the classical theory of dispersion and absorption. This is required by a consequent quantum theory, by a complete vagueness of the problem of the nature of damping constant, etc. Still we consider that the question of the physical simplicity or complexity of an absorption-band can be solved independently of this or other modification of the theory of absorption. The way of solution is already indicated; it is an experimental determination of coefficients characterizing the secondary processes of absorption inside the considered band.

Einstein's theory of the simplest photochemical reactions [*] leads to the result that the coefficient of the velocity of reaction must be inversely proportional to the frequency of the active light. Considering in accordance with modern theories the fluorescence as a production of light accompanying the simple reaction of dissociation, we can hypothetically apply this conclusion to fluorescence. Therefore we can expect the following dependence of κ upon λ inside a simple absorption-band:

$$\kappa = a \,.\, \lambda,$$

where a is a constant. For a complex band, κ must be a totally different function of λ.

Thus we can interpret the experimental results of computation of κ on the following lines:—

(*a*) If $$\kappa = \phi(\lambda), \quad \ldots \ldots \quad (3)$$

where ϕ is a more or less complicated function of λ, the absorption-band is a physically complex one.

(*b*) If $$\kappa = a \,.\, \lambda, \quad \ldots \ldots \quad (4)$$

the band is a simple one and the theory of Einstein is true.

(*c*) If $$\kappa = \text{const.}, \quad \ldots \ldots \quad (5)$$

the band is a simple one and the theory of Einstein is not true.

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[*] A. Einstein, *Journ. d. Phys.* V. iii. p. 277 (1913).

EXPERIMENTS.

As has been already mentioned, Nichols and Merritt found that the specific fluorescence of Resorufin and Eosin increases towards long wave-lengths. The scope of the present investigation is to state how general is this result. It is of some interest to note that when this increase is a general rule we can give a simple explanation to the law of Stokes. From this standpoint, the fluorescence is excited chiefly or exclusively by the absorption in a small band situated towards long wave-lengths relatively to the resulting maximum of a complex band.

The appearance of the curve for Resorufin suggests that the band is complex, while in addition to the principal maximum, there are three secondary maxima from the side of the short waves *. The band of absorption of Eosin investigated by Nichols and Merritt differs considerably from that of Eosin studied by us (fig. 3). Unfortunately, among six Eosins at our disposal we did not find a dye very closely resembling the Eosin of Nichols and Merritt. These authors excited fluorescence by a Nernst glower which took the place of the slit of a large spectrometer. The narrow regions in the spectrum thus formed were used in exciting the solution studied. The intensity of fluorescence so excited was evidently very feeble; this can explain the very considerable deviations of computed points, especially in the case of Eosin.

The diminution of errors of observation had a considerable significance for us when proposing to test the equation of Einstein (4), where the systematical deviations do not exceed 15–19 per cent. in the conditions of the experiment. Therefore it was necessary to increase the intensity of fluorescence and to avoid the errors in determining the wave-lengths of the exciting light which are almost inevitable in a prismatical resolving of light, especially in the yellow-red part of the spectrum. Therefore we applied, instead of monochromatic light, the light transmitted through the light-filters quantitively measured.

Let us presume that the energy of the exciting source of light in the interval of wave-lengths $\lambda \ldots \lambda + d\lambda$ shall be I_λ. The measurement of intensity of fluorescence is made in that place in the vessel with the fluorescing solution where light has already passed the layer of thickness d. The coefficient of absorption of solutions studied in the given

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[*] E. Nichols and E. Merritt, *loc. cit.*

interval of waves is xc, where c is concentration. Following (1), the intensity of fluorescence in the named point of vessel will be

$$\kappa_\lambda \, . \, \mathrm{I}_\lambda \, . \, xc \, . \, e^{-xcd}.$$

Let further a light-filter be placed between the source of light and the vessel transmitting the part of light $f(\lambda)$. In this case the integral intensity of fluorescence will be expressed by

$$\mathrm{F} = \int_{\lambda_1}^{\lambda_2} \kappa_\lambda \, . \, \mathrm{I}_\lambda \, . \, f(\lambda) \, . \, xc \, . \, e^{-xcd} \, . \, d\lambda, \quad . \quad . \quad (6)$$

where λ_1, λ_2 are the practical limits of the disappearance of the function

$$\mathrm{I}_\lambda \, . \, f(\lambda) \, . \, xc \, . \, e^{-xcd}$$

(these limits depend evidently upon the applied light-filter) and κ_λ is the specific fluorescence (2).

In the experiments of Nichols and Merritt and in the theory of Einstein, κ_λ is an increasing function of λ. In both cases we can apply to (6) the theorem of the middle value of a definite integral—*i.e.*, we have

$$\kappa' = \frac{\mathrm{F}}{\int_{\lambda_1}^{\lambda_2} \mathrm{I}_\lambda \, . \, f(\lambda) \, . \, xc \, . \, e^{-xcd} \, . \, d\lambda}, \quad . \quad . \quad . \quad . \quad (7)$$

where κ' is the middle value of κ_λ corresponding to λ', lying between λ_1 and λ_2. When κ_λ is a linear function (as follows from the theory of Einstein and also from Nichols and Merritt's experimental results for Eosin and also in a long interval for Resorufin), and when the subintegral function in (7) is symmetrical relatively to

$$\lambda = \frac{\lambda_2 - \lambda_1}{2},$$

then it is easy to prove that κ' corresponds to λ, through which passes the ordinate halving the area

$$\Phi = \int_{\lambda_1}^{\lambda_2} \mathrm{I}_\lambda \, . \, f(\lambda) \, . \, xc \, . \, e^{-xcd} \, . \, d\lambda. \quad . \quad . \quad . \quad (8)$$

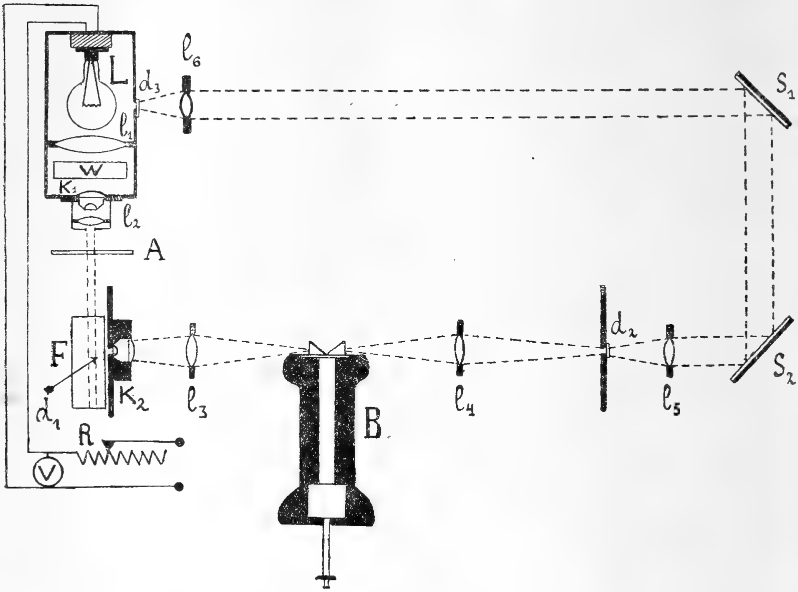
In cases when the subintegral function is only approximately symmetrical (with which we are chiefly concerned), κ' corresponds only approximately to the halving ordinate of area ϕ. The formula (7) can be applied evidently also in the case where κ_λ has a maximum inside of the band of absorption if the limits $\lambda_2 - \lambda_1$ are sufficiently narrow.

The values of I_λ, $f(\lambda)$, xc, d were measured, e^{-xcd} was calculated. The area Φ was determined by graphical integration by means of an Amsler's planimeter. The error of each separate measurement necessary for the calculation of ϕ is the usual spectro-photometrical one.

The method of light-filters simplifying observations unfortunately complicates calculations exceedingly.

The installation of apparatus is given in fig. 1. The image of one of the wires of Philips's lamp ($\frac{1}{2}$ W., 200 candles, 106 volt) is projected by a large condenser l_1 through a vessel W with water upon the aperture of the Zeiss aplanatic condenser K_1. Through the lens l_2 passes a practically parallel bundle of light of a considerable intensity, and through the light-filter A enters a plane-parallel vessel F containing the fluorescing solution. Through the aperture d_1 in the screen the light of fluorescence is projected by means of another aplanatic condenser K_2, the lens l_3, and the auxiliary prism upon the slit of a spectro-photometer of König and Martens, B. The passage of rays from the same lamp L entering in the second slit of B is seen in fig. 1.

Fig. 1.



The voltage can be regulated by means of a rheostat R. A trial has shown that the change of voltage from 100 to 110 does not influence perceptibly the relation of intensities measured by the spectro-photometer. The vessel F by means of slides not represented in the figure can be moved with a micrometrical screw along the screen. In such a way *d* can be regulated. The same installation served for measurement of the absorption spectra of the dyes studied, light-filters, and for determining the distribution of energy of the exciting light. For the measurement of absorption of light-filters, the widths of the slits of the spectro-photometer were taken as 0·1–0·2 mm. (measurements of intensity of fluorescence were made with open slits, *i. e.* the spectro-photometer served rather as a photometer). Instead of vessel F a prism of total reflexion was put and the aperture d_1 was closed by a ground glass. Thus the light passing light-filter A enters the spectro-photometer. The second measurement was made without a light-filter. Hence the coefficient of absorption was determined as usual. The absorption of solutions of dyes was measured in different ways : (1) by means of a vessel with Schultz's body; (2) by an immediate installation of an absorption vessel in the passage of the parallel light-bundle between l_6 and S_1 ; (3) for determining the slopes of the curves of absorption the measurements were made in vessels of considerable thickness (6–8 cm.).

The Distribution of Energy.

A Hefner's candle was used as a standard. Its distribution of energy in the visible spectrum has been carefully measured by Ångström [*], and can be expressed quite precisely through the formula of a grey radiation :

$$I_\lambda = 0{\cdot}0160 \, . \, \lambda^{-5} \, . \, e^{-\frac{7{\cdot}85}{\lambda}}, \quad . \quad . \quad . \quad . \quad (9)$$

(λ in microns). The formula was frequently tested. The measurements of Nichols & Merritt and Coblentz [†] show that the perceptible deviations begin only in the red region of the spectrum, approximately from 605 $\mu\mu$: *i. e.*, behind the limits of interval studied by us. We can evaluate the exactness of (9) according to the difference of the integral radiation of the Hefner's candle, measured frequently, and

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[*] K. Ångström, Phys. Rev., I. xvii. p. 302 (1903).

[†] *Cf.* C. L. Nichols and E. Merritt, 'Studies in Luminescence,' p. 178 (Washington, 1912).

the integral radiation calculated by means of the law of Planck:

$$I_\lambda = \frac{2c^2\lambda}{\lambda^5} \cdot \frac{1}{e^{\frac{ch}{\kappa\lambda T}} - 1},$$

with constants changed on the basis of formula (9). The measured value of the integral radiation is

$$2{\cdot}15 \,.\, 10^{-5} \frac{\text{gr. cal.}}{\text{sec. cm.}^2},$$

the calculated value

$$2{\cdot}74 \,.\, 10^{-5} \frac{\text{gr. cal.}}{\text{sec. cm.}^2}.$$

The deviations lie, according to the above, in the red and infra-red part of the spectrum.

For the determination of distribution of energy of our source, the prism of total reflexion was put instead of the vessel F, the aperture d_1 was closed by a ground glass, and a comparison was made between the intensity of the light illuminating the ground glass with that of the light entering the right slit of the spectro-photometer. Afterwards the prism was removed, and by means of an achromatic lens the image of the flame of a Hefner's candle was projected upon the ground glass in such a way that the part of the flame 1·5 cm. above the wick was projected on the aperture d_1*. The curve of relations of measured intensities of source and candle, multiplied by (9), gives the distribution of energy of our source of light. The curve determined in such a way satisfies sufficiently the formula of grey radiation:

$$I_\lambda = Q \,.\, \lambda^{-s} \,.\, e^{-\frac{2\cdot67}{\lambda}} \quad \ldots \ldots \quad (10)$$

In Table I. are given the values of I_λ measured with those calculated by (10), wherein Q is taken as $4{\cdot}710 \,.\, 10^3$.

TABLE I.

λ	T_λ meas.	T_λ calc.
0·410	0·125	0·133
0·435	0·258	0·235
0·455	0·380	0·345
0·473	0·480	0·489
0·490	0·660	0·645
0·515	0·880	0·905
0·548	1·325	1·350
0·565	1·588	1·560
0·580	1·870	1·910
0·590	2·080	2·050

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* A. Becker, *Ann. d. Phys.* xxviii. p. 1029 (1909).

Measurements were repeated several times during our work, giving always the same result.

We used light-filters, partly coloured glasses, partly coloured films put between two glass plates. Some light-filters were prepared by us in collodion and gelatine films on glass. The curves of absorption of light-filters were measured at least twice.

Dyes.

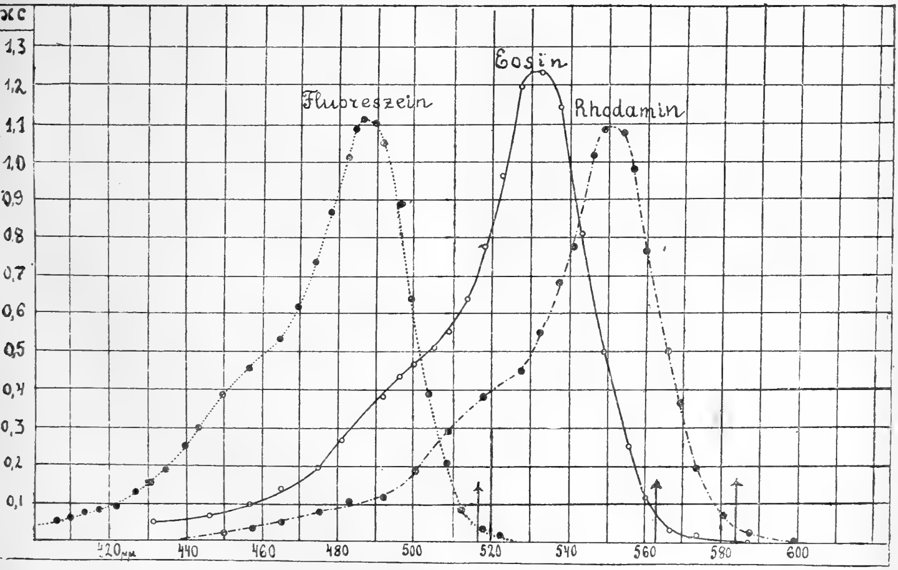
The fluorescing dyes were selected so that their bands of absorption covered the whole region accessible to visual investigation from 400 $\mu\mu$ to 600 $\mu\mu$. Most careful measurements were made with water solutions of the following dyes :—

Fluorescein (Ferrein) + KOH $9{\cdot}7 \,.\, 10^{-6} \frac{\text{gr.}}{\text{cm.}^3}$ and $4{\cdot}85^{-7} \frac{\text{gr.}}{\text{cm.}^3}$.

Eosin S extra C. (Bayer) ... $1{\cdot}2 \,.\, 10^{-5} \frac{\text{gr.}}{\text{cm.}^3}$.

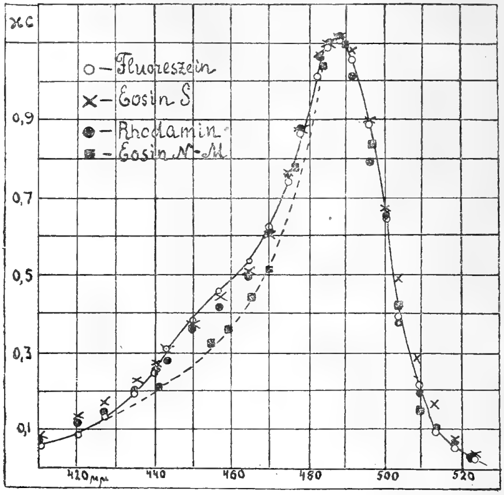
Rhodamin B extra (Bayer) ... $1{\cdot}4 \,.\, 10^{-6} \frac{\text{gr.}}{\text{cm.}^3}$.

Fig. 2.



Eosin S gives a rather weak fluorescence ; still it was the only one whose band of absorption followed sufficiently that of the Eosin studied by Nichols and Merritt. In fig. 2 are given the curves of absorption of all three dyes. The ordinates of Fluorescein correspond in the figure to 0·163 $\varkappa c$ and for two other dyes $\varkappa c$. The curves are perfectly monotypical, differing only in the different situation of maximum and the absolute value of $\varkappa c$. This can be proved by a superposition of all three curves. In fig. 3 the curve of

Fig. 3.



Eosin is removed to a distance of 45 $\mu\mu$: *i. e.*, the interval separating the maximum of Fluorescein and Eosin. The curve of Rhodamin is removed to a distance of 65 $\mu\mu$. The ordinates of maxima of all curves are reduced to the same value. On the same figure are marked the points corresponding to Eosin of Nichols and Merritt, maximum removed to a distance of 38 $\mu\mu$. The established regularity allows of several conclusions being drawn:—

1. All dyes studied by us have the same mechanism of absorption in the visible part of absorption.

2. The coefficient of absorption is sufficiently approximated by

$$\varkappa c = f(\lambda - \lambda_0),$$

which is in contradiction with the classical theory for the simple band and likewise for a complex one.

3. The invariability of the form of the curves by removing their maxima to a distance of 65 $\mu\mu$, serves as a criterion of the optical cleanness of our preparations.

4. The same fact serves, of course, as an indirect indication of physical simplicity of the bands of absorption studied.

The intensity of fluorescence for every dye is measured with 8 to 10 light-filters with a constant thickness of absorbing layer *d*. For Fluorescein and Eosin two measurements were made with different *d*. Every measurement was repeated at least three times on different days.

For ascertaining the amount of diffused light in the measured light of fluorescence, the solution of dye in the vessel F was replaced by pure water. In all cases the quantity of the diffused light was not more than 1 per cent. : *i.e.*, could be disregarded.

Results.

We abstain from the reproduction of lengthy tables with elements necessary for graphical calculations of Φ on the basis of (8). The values of I_λ, xc, e^{-xcd}, $f(\lambda)$ were taken from experimental curves for every 5 $\mu\mu$. As an example of the subintegral function so obtained we include fig. 4, representing nine curves obtained for Eosin with different light-filters. Beside every curve is given the value of Φ, obtained by a graphical integration in the relative units, the observed value of intensity of fluorescence, also in relative units, and the relation

$$\kappa=\frac{\phi}{\mathrm{F}}.$$

As shown in the figure, the curves are approximately symmetrical. According to the above mentioned, we can consider that κ so computed corresponds more or less to the wave-length through which passes the halving ordinate of area Φ. On every curve this ordinate is marked by a dotted line. The Tables II., III., IV. contain the following data :—(1) light-filter used, (2) the value of λ through which passes the halving ordinate, (3) F, (4) ϕ, (5) κ. The tables give also *d* and concentration. The tables correspond to the most careful measurements.

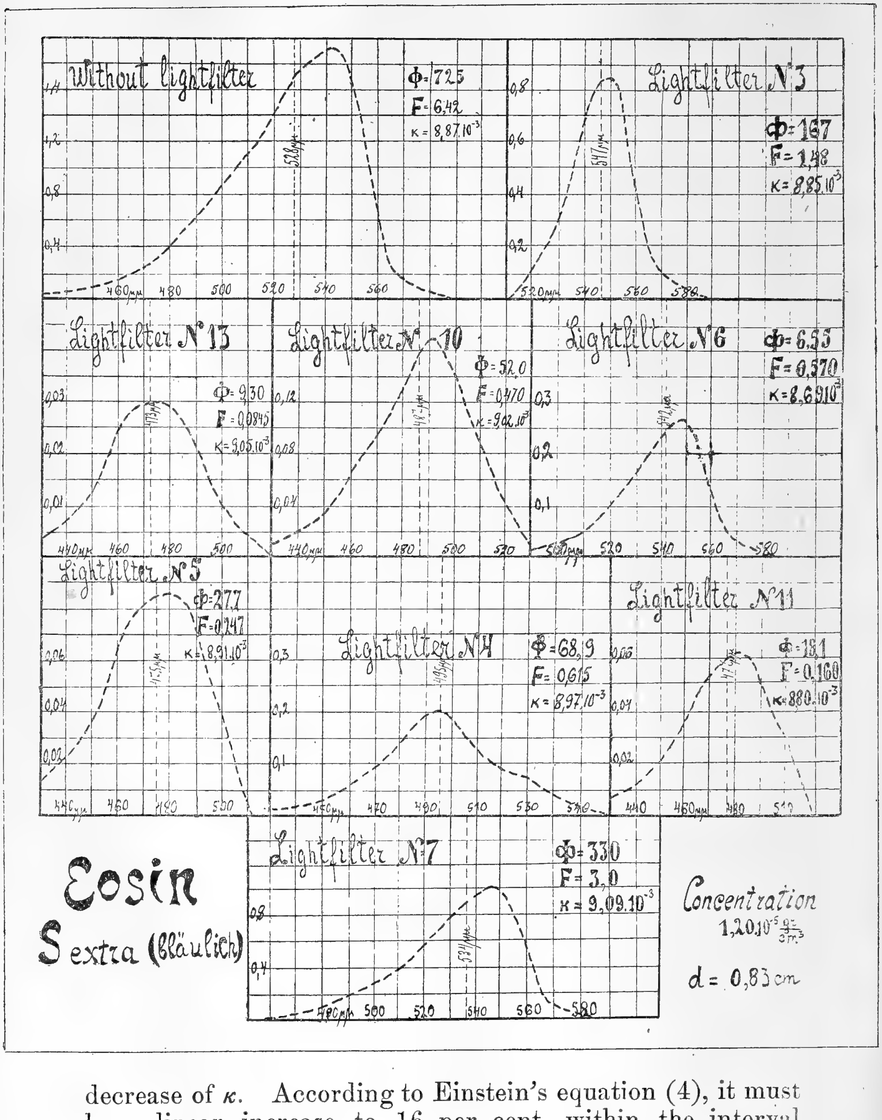
Table II.

Fluorescein. $c=3{\cdot}7\,.\,10^{-6}\,\frac{\text{gr.}}{\text{cm.}^3}$; $d=0{\cdot}80$.

	λ.	F.	ϕ.	κ.
5	446 $\mu\mu$	2·940	61·0	4·81 . 10^{-2}
14	448	0·0579	1·23	4·70
13	449	0·920	19·3	4·77
10	453	3·70	7·50	4·93
0	482	14·60	296	4·88
7	506	3·62	7·45	4·86
8	510	4·90	97·0	5·05
3	519	0·218	4·55	4·80

From Table II. it is seen that κ is constant in the limits of errors of measurement of ϕ and F. The greatest deviation reaches 7 per cent. There is no perceptible increase or

Fig. 4.



decrease of κ. According to Einstein's equation (4), it must be a linear increase to 16 per cent. within the interval 446 to 519 $\mu\mu$.

TABLE III.

Eosin S extra. $c=1{\cdot}20\,.\,10^{-5}\frac{\text{gr.}}{\text{cm.}^3}$; $d=0{\cdot}83$.

	λ.	F.	φ.	κ.
13	473 μμ	0·0845	9·30	$9{\cdot}05\,.\,10^{-3}$
5	475	0·247	27·7	8·91
11	477	0·160	18·1	8·80
10	487	0·470	52·0	9·02
4	495	0·615	68·9	8·97
0	528	6·42	725	8·87
7	534	3·00	330	9·09
6	542	0·570	6·55	8·69
3	547	1·48	167	8·85

TABLE IV.

Rhodamin B extra. $c=2{\cdot}4\,.\,10^{-6}\frac{\text{gr.}}{\text{cm.}^3}$; $d=0{\cdot}83$.

	λ.	F.	φ.	κ.
5	478 μμ	0·364	10·6	$3{\cdot}43\,.\,10^{-2}$
10	492	8·25	23·9	3·46
4	513	1·67	48·5	3·45
9	544	11·4	318	3·58
0	547	29·1	809	3·60
7	552	15·8	447	3·53
3	559	12·6	339	3·70
2	579	1·05	29·2	3·60

Table III. gives the same result for Eosin. The deviation of κ reaches 5 per cent.; according to Einstein, there must exist the increase of 16 per cent.

For Rhodamin there is a small increase of κ with wave-length, which lies still inside the limit of errors of experiment. The greatest deviation is 8 per cent. This systematic deviation can be possibly explained by the existence of some discordance between the Ångström equation (9) and the true distribution of energy in the spectrum of the Hefner's candle. According to Einstein, the value of κ must increase in this case by 21 per cent.

In other less careful measurements of κ the deviations amounted to 10 to 14 per cent.

Conclusions.

(1) Within the limits of errors of observation the specific fluorescence of our dyes is independent of λ within their band of absorption.

(2) According to all above-mentioned, this result is equivalent to the conclusion that the curves of absorption of our dyes are physically simple ones.

(3) The theory of Einstein is not confirmed, but the deviations required by this theory are so small that they exceed only a little the experimental errors, and we are unable to make a definite statement.

(4) The intensity of fluorescence radiated by a definite molecular resonator depends only upon the value of the absorbed energy and upon the mechanism of the resonator. In the case of an excitation by a white light we can therefore write

$$F=\kappa\int_{\lambda_1}^{\lambda_2} I_\lambda \, . \, xc \, . \, e^{-xcd} \, . \, d\lambda. \quad . \quad . \quad . \quad . \quad (11)$$

(5) The result of Nichols and Merritt shows probably only the physical complexity of bands of dyes studied by these authors.

This work was carried out in the Physics Department of the Scientific Institution of Moscow, to the Director of which, Prof. Dr. P. P. Lasareff, I am much indebted for much valuable help and for his interest during the course of the work.

XXX. *Notes on Hertz's Theory of the Contact of Elastic Bodies. By* W. B. Morton, *M.A., and* L. J. Close, *M.A., Queen's University, Belfast*[*].

1. *Introduction.*

THE elastic problem of the deformations and stresses which arise when two bodies, having continuous curvature, are pressed together was solved by Hertz[†] in a classical memoir. He showed that the area of contact is, in general, an ellipse, and that the displacement in the neighbourhood of the contact could be expressed by means of potential functions belonging to a certain distribution of surface-density on this ellipse: viz., that reached as the limit of a uniform solid ellipsoid. In view of the complicated nature of the mathematics, Hertz contented himself with establishing some general conclusions and with drawing a diagram of the lines of principal stress which was partly conjectural and which was afterwards found to be erroneous

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[*] Communicated by the Authors.

[†] Hertz, Miscellaneous Papers (Engl. trans.) p. 146. See Love, 'Elasticity' (3rd ed.), p. 191.

in some of its features. The subject was further developed by Huber* for the contact of two spherical surfaces, in which case the potentials can be expressed in finite forms. For this simple case the question of the correct forms of the lines of principal stress was settled by Fuchs†, who obtained the result by carrying out a laborious process of arithmetical integration.

The present work had its origin in an endeavour to apply the method of expansion in zonal harmonics in order to obtain numerical values for the stresses, etc., in Huber's case of axial symmetry. The formulæ of Huber contain an elliptic co-ordinate, the parameter of the spheroid through the point which is confocal with the circle of contact. This is inconvenient for purposes of calculation. On the other hand, a good deal of labour was found to be needed in evaluating the series to which we were led, so it is doubtful whether one method has an advantage over the other in this respect. It does not, therefore, seem worth while to reproduce the details of our analysis; but some of the results obtained, with regard to the magnitudes and directions of the principal stresses, may be of interest as adding a little to what is already known. We give graphs for the stresses along lines running from the centre of contact in directions making angles 0, 30°, 60°, 90° with the normal.

A further note is added on the limiting forms assumed by the lines of principal stress at a distance from the contact. It is shown that the characteristic features of these curves, as discovered by Fuchs, can be simply deduced from the solution given by Boussinesq of the problem of a body acted upon by a pressure concentrated at a point on an otherwise free plane boundary.

2. *Outline of Method.*

Let the axis of z be the inward normal to one of the bodies at the centre of the circle of contact. Suppose a distribution of matter on this circle equivalent to an oblate spheroid of vanishing axis, the whole mass of the distribution being equal to P, the normal force with which the bodies are pressed together. This makes the surface-density at distance r equal to

$$3\mathrm{P}(a^2-r^2)^{\frac{1}{2}}/2\pi a^3,$$

where a is the radius of the circle. Let ϕ be the ordinary inverse potential of this distribution and χ the logarithmic

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* Huber, *Ann. d. Phys.* vol. xiv. p. 153 (1904).

† Fuchs, *Phys. Zeitschr.* vol. xiv. p. 1282 (1913).

potential $\int \log(z+r)\,dm$. Hertz showed that $4\pi\mu \times$ (displacement) is the resultant of the two vectors

$$(1)\quad -\text{slope}\{2\phi+(1-2\sigma)\chi\},$$
$$(2)\quad (1-\sigma)\phi, \text{ parallel to the normal,}$$

where $\mu =$ rigidity, $\sigma =$ Poisson's ratio.

From this the strain-components can be obtained in any chosen system of co-ordinates, *e. g.* polars $(r\ \theta\ \phi)$ or cylindricals $(\varpi\ z\ \phi)$. It was found most convenient to use a rather unorthodox combination of these, the cylindrical components being expanded in polar series. The advantage of the $(\varpi\ z\ \phi)$ system lies in the relation to the fixed direction z. The expressions for the components contain the potentials χ, $\frac{\partial\chi}{\partial z}=\phi$, $\frac{\partial\phi}{\partial z}$, $\frac{\partial^2\phi}{\partial z^2}$. These are expanded as zonal harmonic series in powers of r/a and a/r.

Partial differentiation with respect to ϖ is replaced by $\frac{\partial}{\partial r}$ and $\frac{\partial}{\sin\theta\partial\theta}$, and so ultimately power-series are obtained whose coefficients involve P_n, P_n', $\cos\theta P_n$, $\cos\theta P_n'$. Having tables of P_n we can tabulate the other functions, for a chosen value of θ and sufficient range of n, by using the "recurrence-formulæ."

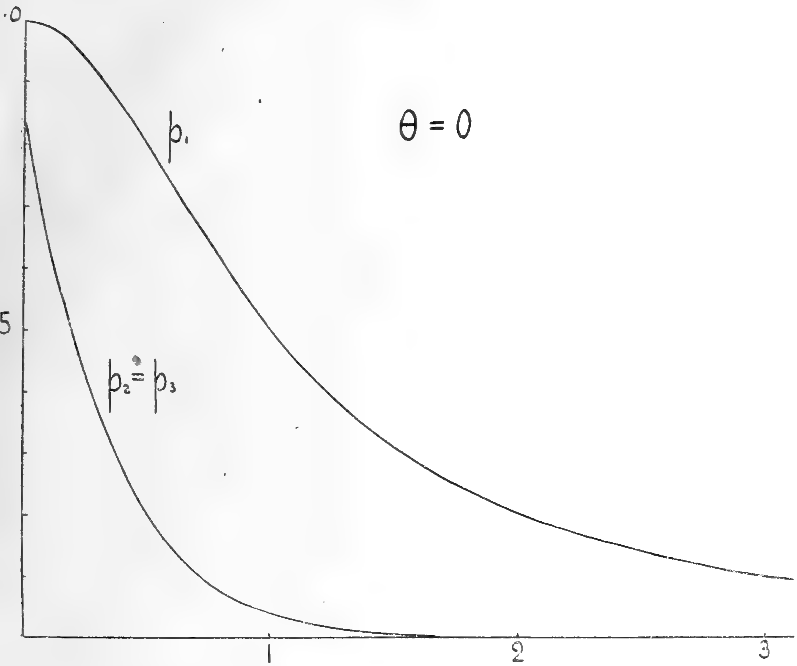
Numerical values for the strain-components were thus obtained for a succession of values of r, less than a and greater than a, by using the ascending and descending series respectively. When these were plotted against r it was found easy to connect the two portions of the curves across the value $r=a$. This was done for $\theta=0$, 30°, 60°, 90°. Poisson's ratio was throughout the work taken as $\frac{1}{3}$, the value used by Hertz and Fuchs. From the strains the cylindrical components of stress were calculated, and finally the magnitudes and directions of the principal stresses at points lying along the four directions from the centre of contact. The results are shown in figs. 1, 2, 3, 4.

3. *Graphs of Principal Stresses.*

On these diagrams the abscissa is distance from the origin, the radius of the circle of contact being taken as unit. The greatest principal pressure p_1 is that which passes into the normal pressure at the origin. Its value there is taken as the unit for ordinates; it is one and a half times the average pressure exerted over the area of contact. The other principal pressure in the plane through the axis is p_2, and the pressure perpendicular to this plane ("hoop-pressure") is p_3.

Along the normal (fig. 1) the transverse pressure begins with five-sixths of the magnitude of the normal pressure; it decreases rapidly and changes to a tension at distance 1·67 × a. The tension beyond this distance is too small to be shown on the diagram.

Fig. 1.



It is easy to deduce these results from the general theory. It can be shown that, on the axis of z, we have

$$2\pi p_1 = z\frac{\partial^2\phi}{\partial z^2} - \frac{\partial\phi}{\partial z}.$$

(The same expression represents the (zz) pressure at any point; it is independent of the elastic constants of the body.)

When there is symmetry round the axis

$$4\pi p_2 = -z\frac{\partial^2\phi}{\partial z^2} - (1+2\sigma)\frac{\partial\phi}{\partial z}.$$

It follows that, for $z=0$, $p_2/p_1 = \sigma + \frac{1}{2}$.

At a great distance from the origin, ϕ approaches the value P/z, and the limiting forms for the pressures become

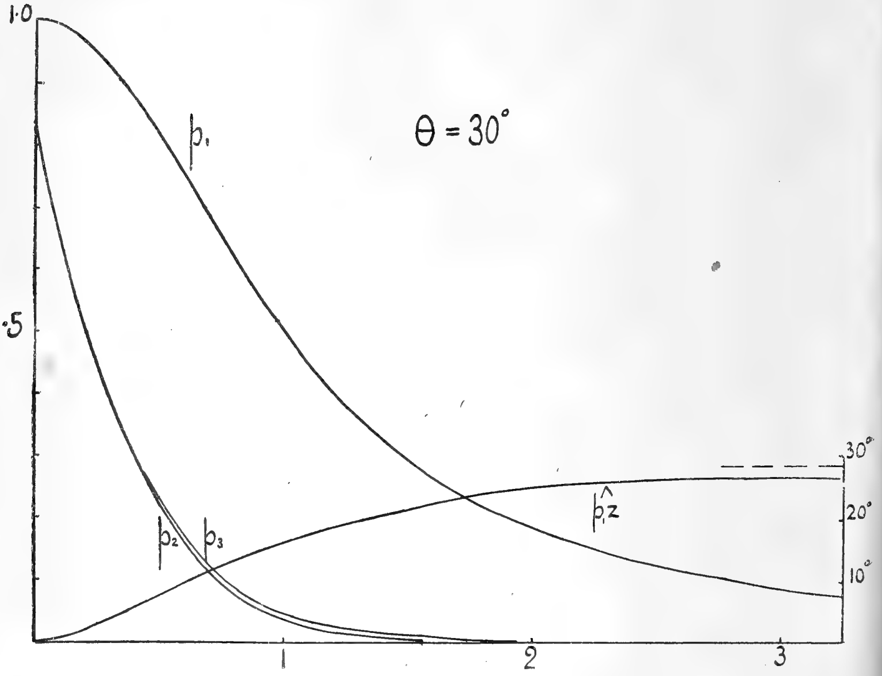
$$2\pi p_1 = 3z^{-2},$$

$$4\pi p_2 = -(1-2\sigma)z^{-2},$$

so $-p_2/p_1$ approaches $\frac{1}{6}(1-2\sigma)$.

Figs. 2 and 3 show that as the normal is departed from the hoop-pressure p_3 becomes the greater of the two subordinate stresses. Along the line $\theta=30°$ both these stresses change to small tensions, p_2 at $r=1·56\times a$, p_3 at $r=1·95\times a$. Along $\theta=60°$ the hoop-stress remains a pressure at all distances; the other changes to tension at $r=1·35\times a$.

Fig. 2.



The directions of the principal axes of stress and strain are shown by the curve for the angle between p_1 and the normal. It will be seen that, as the distance from the contact increases, the direction of the chief principal stress approaches that of the radius vector from the origin, but does not tend to coincide with it. The broken lines at the right of the figures show the limiting directions of p_1, making an angle with the normal of 28° 21′ instead of 30°, 56° 3′ instead of 60°.

Fig. 3.

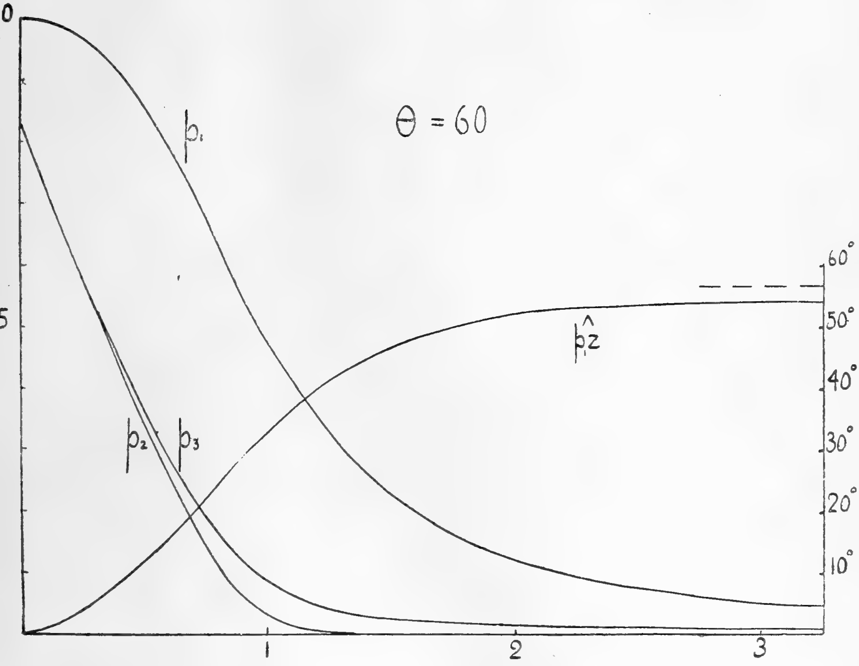
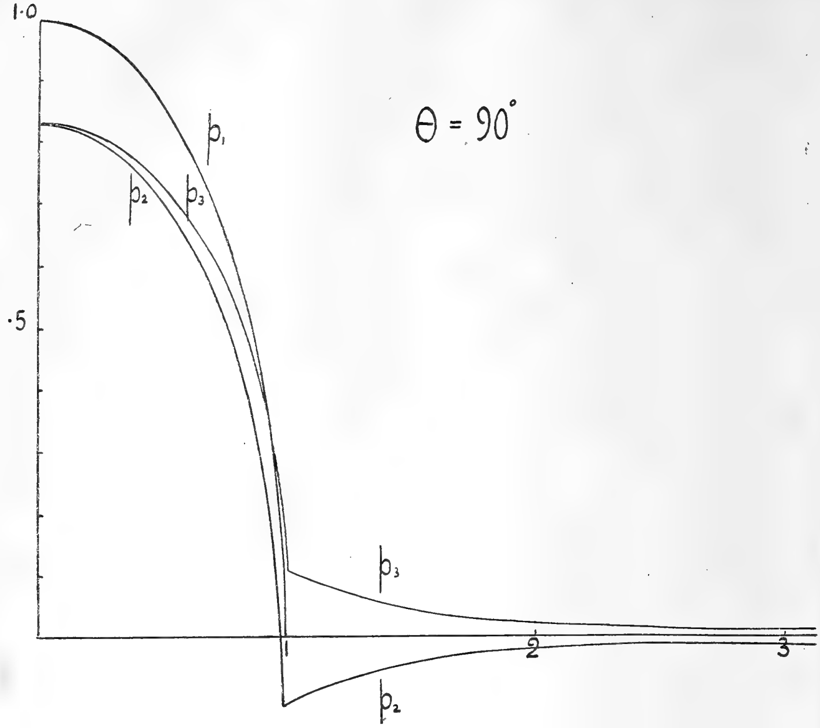


Fig. 4 shows the state of affairs on the boundary (supposed to have only small curvature). Inside the area of contact the three principal pressures are of comparable magnitudes. Outside this area the normal pressure of course vanishes, while the tension across the radius is equal in magnitude to the pressure across it. This is on account of the vanishing of the dilatation and the reduction of the strain and stress to pure shears. On the general theory the expression for the dilatation is

$$\frac{\partial\phi}{\partial z}\Big/2\pi(\lambda+\mu),$$

which obviously vanishes on the plane of the supposed attracting distribution.

Fig. 4.



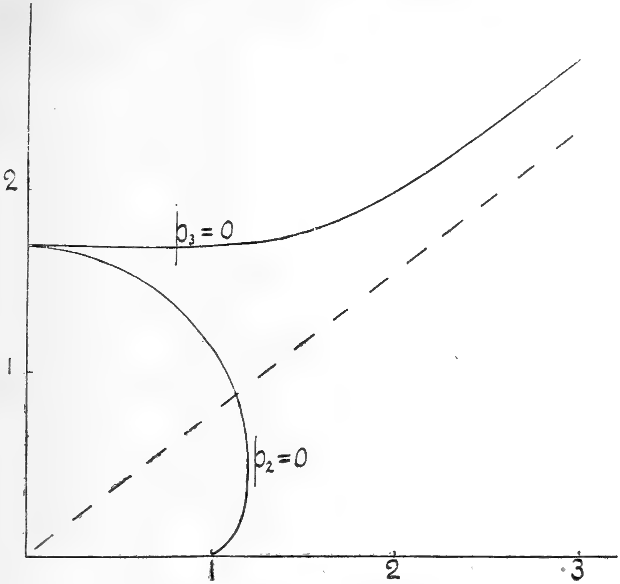
4. *Distribution of Smaller Stresses.*

There are two questions suggested by these graphs which require further examination. The first is the distribution of the stresses p_2 p_3, and in particular the loci in the body at which they vanish and change sign. As the result of some further calculation, these loci are found to have approximately the forms shown on fig. 5. There is a region, surrounding the origin and based on a circle very slightly smaller than the circle of contact, within which all three principal stresses are pressures. The boundary of this region is marked $p_2=0$. Springing from the top of this is the locus $p_3=0$, above which both p_2 and p_3 are negative; below it, and outside the former region, there is a hoop-pressure, while the smaller principal stress in the axial plane is a tension. The main stress p_1 is everywhere a pressure.

As the area of contact shrinks to a point, the locus $p_2=0$

disappears and $p_3=0$ becomes a cone, one of whose generators is shown by the broken line. This is Boussinesq's case* of pressure at a point. Inside the cone there is hoop-pressure, outside hoop-tension. The angle of the cone is found to be independent of the elastic constants and to satisfy the equation

Fig. 5.



$$\cos^2\theta+\cos\theta=1,$$

giving $$\cos\theta=\tfrac{1}{2}(\surd 5-1),\quad \theta=51^\circ\,50'.$$

In this limiting case, p_2 is everywhere negative.

5. *Lines of Principal Stress.*

The other question suggested is the limiting value approached by the angle between p_1 and the radius vector as r increases in any direction θ. To find this it is sufficient to use the results of the simple case just referred to, in which the area of contact is regarded as a point, and $\phi=\mathrm{P}/r$. On working out the strain-components in polar co-ordinates the inclination ψ of the principal stress p_1 to the radius vector is found to be given by the equation

$$\tan 2\psi=2(1-2\sigma)\sin\theta\cos\theta/\{(5-4\sigma)\cos^2\theta+3\cos\theta-(1-2\sigma)\},$$

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* Love, 'Elasticity,' p. 189.

As θ increases from 0 to 90°, ψ also runs through the same range but the variation of ψ is marked by a sudden transition from a slow and steady increase over most of the range to a very rapid increase near the end. For example, with $\sigma=\frac{1}{3}$ we find

$$\psi=10^\circ\,28' \text{ for } \theta=80^\circ,$$

$$\psi=90^\circ \qquad \text{for } \theta=90^\circ.$$

This means that p_1 keeps near the direction of r as the normal is departed from, being inclined to r on the side of the normal ; but just before the radius vector reaches the boundary there is a rapid tilting of the direction of p_1, bringing it perpendicular to r, *i.e.* to the boundary. Along with this, of course, the magnitude of p_1 becomes zero.

For the purpose of obtaining the forms of the lines of principal stress, it is convenient to tabulate $(\theta-\psi)$, the inclination of p_1 to the fixed direction of the normal. This is found to have a maximum value at about $\theta=79^\circ$. The lines of principal stress are thus two families of similar curves, intersecting at right angles and having points of inflexion along the radii $\theta=\pm79^\circ$. Since the direction of the tangent is known for each point of the plane, an approximation to the forms of the curves can be found*. The result is shown on fig. 6. The forms are similar to those given by Fuchs † for the outer curves in the more general case. The broken line drawn to the intersection of the two curves is the locus of inflexions.

A remark may be added about the displacements in this case. In the account of Boussinesq's solution given by Love ‡ it is mentioned that the particles move towards or from the line of action of the applied force according as they lie outside or inside a cone whose angle is given by

$$\cos^2\theta+\cos\theta=1-2\sigma.$$

It may not have been noticed that the differential equation of the "lines of displacement" can be integrated in finite form. Using polars, the differential equation is

$$dr/r=-d\theta(1+\cos\theta)\{4(1-\sigma)\cos\theta-(1-2\sigma)\}/\sin\theta\{(3-4\sigma)\cos\theta+2(1-\sigma)\},$$

with the integral

$$-\log r=\text{A}\log(1-\cos\theta)+\text{B}\log(\cos\theta+\text{C})+\text{const.},$$

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* d'Ocagne, *Calcul Graphique et Nomographie*, p. 155.

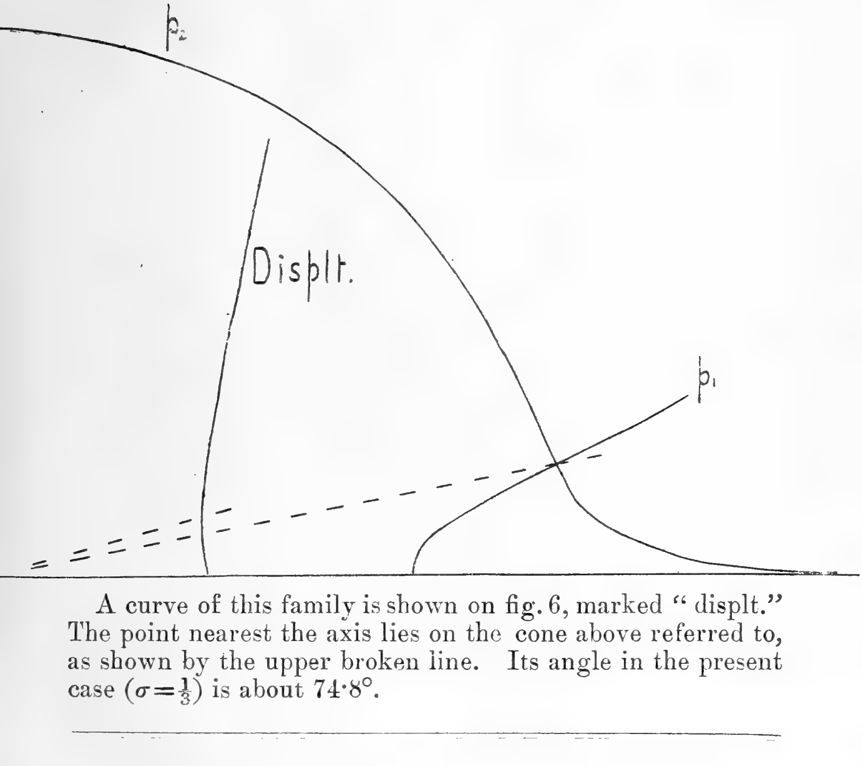
† See Love, *loc. cit.* p. 196.

‡ *Loc. cit.* p. 190.

where

$$A=(3-2\sigma)/(5-6\sigma),$$
$$B=(11-26\sigma+16\sigma^2)/(5-6\sigma)(3-4\sigma),$$
$$C=2(1-\sigma)/(3-4\sigma).$$

Fig. 6.



A curve of this family is shown on fig. 6, marked "displt." The point nearest the axis lies on the cone above referred to, as shown by the upper broken line. Its angle in the present case ($\sigma=\frac{1}{3}$) is about 74·8°.

XXXI. *Natural Convective Cooling of Wires.*

By A. H. Davis, *B.Sc.*[*]

[From the National Physical Laboratory.]

(1) *Introduction.*

THE object of this paper is to investigate the apparent discrepancy between published data for the natural convective cooling of wires and the hydrodynamical theory of the phenomenon.

"Convective cooling" is taken to refer to the total heat

[*] Communicated by the Author.

transfer from a hot body by the medium of a fluid moving past the surface. Such cooling is said to be "natural" or "free" when the fluid is still except for the streams set up by the heat from the hot body itself.

The theory involves the dilatability of the fluid, the hydrodynamical equations of motion, the Fourier equations of heat-flow, and the appropriate boundary conditions. From this point of view Boussinesq* has studied both natural and forced convection for similar bodies immersed in an infinite inviscid fluid. His formulæ may also be derived from the principle of similitude by simple consideration of the variables involved, and may be extended to viscous fluids by the same means. The following formula is obtained for the heat loss by natural convection from similar bodies similarly immersed in viscous fluids.

$$hl/k\theta = \mathrm{F}(c^2gl^3a\theta/k^2)f(cv/k), \quad . \quad . \quad . \quad . \quad (1)$$

where

h = heat-loss per second per unit area of the body,
k = thermal conductivity of the fluid,
c = capacity for heat of the fluid per unit volume,
θ = temperature excess of the body,
a = coefficient of density reduction of the fluid per degree rise of temperature,
g = acceleration due to gravity,
l = linear dimensions of the body.

For a given kind of gas cv/k appears to be constant as required by the kinetic theory, and the formula becomes simpler

$$h = (k\theta/l)\mathrm{F}(c^2gl^3a\theta/k^2). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The formula involves an assumption that a and g always occur as a product, that is, that the expansion of the fluid is negligible, except in so far as it alters the *weight* of unit volume, and thus supplies the necessary driving force for the convection currents. This restriction may impose limits to the temperature excess for which the formula is applicable for a given series of bodies.

If only the temperature and size of the model are varied, the gaseous constants (c, a, and k) and gravity (g) remaining the same, the formula becomes

$$h = (\theta/l)\mathrm{F}(\theta l^3). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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* Boussinesq, *Comptes Rendus*, cxxxii. p. 1382 (1901).

In a previous paper * where this formula was studied, it was shown that in general, both for forced and for free convection, the hydrodynamic formulæ are in very promising agreement with published data, except in the case of free convection from hot thin wires. The present paper investigates this apparent disagreement.

(2) *Convection loss from wires.*

Experimenters have almost invariably conducted wire experiments at temperatures much higher than those used with larger bodies, and this suggests two possible sources of the apparent failure of the theoretical formula. Firstly, it may be that in this extreme case it is no longer legitimate to assume that "a" and "g" occur only as a product, the mere volume changes of the air now having sensible effect. Secondly, it may be now necessary to allow for the change of the conductivity and specific heat of the fluid due to the temperature rise caused by the hot wire. The present paper shows the remarkable improvement which follows an attempt to allow for this second effect, so that even for thin wires the equation appears to be substantially correct.

The formula may be put in a more convenient form for our purpose. In (1) "h" refers to unit *area*, and if the body is a long cylinder, "h" is obviously unaffected by the length. It readily follows that for long cylinders (diameter d) the heat loss H per unit length per degree temperature elevation is given by

$$H/k = F(c^2 g d^3 a\theta/k^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Writing ν for k/c (since $c\nu/k$ is constant for a given kind of gas) and regarding "a" † and "g" as constant, we have

$$H/k = F(\theta d^3/\nu^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Consequently, if data for the natural convective cooling of long cylinders be plotted on a graph with H/k as ordinate and $\theta d^3/\nu^2$ as abscissa, the result should be a single curve independent of the size of the cylinders, and also of their temperature excess, if appropriate allowance be made for the variation of k and ν with temperature. Further, from the method of its derivation, formula (5) would appear to hold for all fluids for which $c\nu/k$ is the same. For gases the

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* Davis, Phil. Mag. xl. p. 692 (1920).

† The convection currents depend on the density change relative to the density of the *cold* fluid, so that "a" must be regarded as applicable to the cold gas, and independent of the temperature of the wire.

value of this variable appears to depend on the number of atoms in the molecule, and has the same value for the diatomic gases oxygen, hydrogen, and nitrogen as it has for air, so that these gases should give convection results in agreement with the curve for air.

(3) *Method of examination of data.*

Published data have been examined in the light of the formula, and to obtain a convenient tabular summary the following general procedure has been adopted.

The published data have been converted into c.g.s. units, corrected for radiation if necessary, and plotted on a graph from which values have been read off for even values of temperature excess. This gives corresponding values of θd^3 and H.

To obtain $\theta d^3/\nu^2$ and H/k it was necessary to decide on the values of k and ν appropriate to the particular experiment. For a hot wire in air at room temperature (15° C.) the appropriate values are neither those for air at the temperature of the hot wire nor those for air at 15° C. As a first approximation the values actually taken were those for air at the mean of these two temperatures.

In cases where the pressure was not atmospheric allowance has been made as before, and in addition it has been assumed that, as indicated by the kinetic theory of gases, both the conductivity k and the viscosity η are independent of pressure, and consequently the kinematical viscosity ν has been taken as inversely proportional to the pressure of the gas.

In following this general procedure certain auxiliary constants have been used, as explained in the following paragraphs :—

(a) *Radiation correction.*—Data for heat losses are often published in the form of a total loss, radiation being included. Langmuir [*], who used platinum wires, published his data with the radiation eliminated, and in this paper results obtained by other experimenters for platinum surfaces have been corrected, using his values for the emissivity for radiation. For steam pipes, total heat losses given by Petavel have been corrected by the amount attributed by him to radiation, an amount equivalent to $0{\cdot}4\times10^{-12}\times(T^4-T_0^4)$ [†] calories per sq. cm. per sec., where T and T_0

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[*] Langmuir, Phys. Rev. xxxiv. p. 401 (1912).

[†] $5\times10^{-10}(T^4-T_0^4)$ B.T.U. per square foot per hour.

refer respectively to the absolute temperatures of the body and its surroundings.

(b) *Convection constants of gases.*—Below are given data to express the variation of k and ν with temperature.

The viscosity (η) of a gas is given by Sutherland's formula and the density by $\rho=\rho_0\,(273/\mathrm{T})$, where T is the absolute temperature : from these the kinematical viscosity $\nu\ (=\eta/\rho)$ has been derived.

The conductivity (k) has been calculated from the viscosity (η) and the specific heat at constant volume (c_v), using the formula $k/c_v\eta=\text{constant}$, as given by the kinetic theory of gases. Eucken * has shown that the constant has the value 2·50 for monatomic gases and 1·90 for the diatomic gases hydrogen, oxygen, nitrogen, and also for air. The specific heats at high temperature have been obtained from the data given by M. Pier †, who has given formulæ which, for the above gases, may be written $c_v=\mathrm{A}(1+0{\cdot}0002\mathrm{T})$, where A depends on the nature of the gas. Langmuir ‡ adopted this method of calculating conductivity when dealing with heat convection from the point of view of conduction through a film of gas adherent to the hot body.

Thus, for the gases considered,

$$\nu=\eta/\rho, \quad \text{(6)}$$

$$k=1{\cdot}90c_v, \quad \text{(7)}$$

where

$$\eta=\mathrm{KT}^{\frac{1}{2}}/(1+\mathrm{C}/\mathrm{T}), \quad \text{(8)}$$

$$c_v=\mathrm{A}(1+0{\cdot}0002\mathrm{T}), \quad \text{(9)}$$

$$\rho=273\rho_0/\mathrm{T}, \quad \text{(10)}$$

and where the constants have the values given in the following Table :—

TABLE I.

(c.g.s. units.)

	10^6K *.	C *.	A.	$10^3\rho_0$.
Air	15·0	124	0·161	1·293
Hydrogen	6·6	77	2·21	0·09
Oxygen	17·5	127	0·145	1·43

* See Tables by Kaye and Laby, or Fisher, Phys. Rev. xxiv. p. 385 (1907) ; xxix. p. 146 (1909).

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* Eucken, *Phys. Zeit.* xii. p. 1101 (1911).

† Pier, *Z. f. Elektrochem.* xv. p. 536 (1909) ; xvi. p. 899 (1910).

‡ Langmuir, *loc. cit.*

Calculation from these data yields the values for k and ν given in Table II.

TABLE II.

° C.	Air.		Hydrogen.		Oxygen.	
	$10^4 . k$.	ν.	$10^4 . k$.	ν.	$10^4 . k$.	ν.
0	0·55	0·13	3·7	0·9	0·58	·14
17	0·58	0·15	4·1	1·1	0·61	·15
100	0·72	0·23	4·7	1·6	0·75	·24
200	0·86	0·35	5·7	2·4	0·91	·36
300	1·01	0·48	6·5	3·3	1·00	·50
400	1·14	0·62	7·4	4·2	1·20	·66
500	1·27	0·78	8·2	5·3	1·33	·83
1000	1·89	1·76	11·8	11·4	1·97	1·85

(4) *Summary of collected data.*

Following the procedure explained, Tables III. and IV. have been compiled summarizing a wide range of data for convection losses from cylinders. In the experiments of Table III. the wires were used mainly in free air, or in enclosures so large that the free air figure would evidently be obtained. It appears, however, that heat losses from wires in even a small enclosure (a few centimetres diameter) are not different from those obtained in an unlimited medium. In Table III. the results by Ayrton and Kilgour were obtained using water-cooled enclosures 5·08 cm. internal diameter, and they agree excellently with data for similar wires in practically free air, as given by Langmuir and by Kennelly. Table IV. refers to an enclosure of 2·06 cm. diameter, and this is still fairly large compared with the diameter of the wire, and the results for air at one atmosphere agree satisfactorily with the curve derived from data for free air already considered. Results given in the tables are plotted in fig. 1.

The sources from which the summary was compiled are briefly indicated below, the distinguishing letters corresponding with those used in the tables :—

(A) Langmuir * conducted experiments practically in free

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* Langmuir, *loc. cit.*

TABLE III.

Natural Convection from Long Cylinders in Air.

(Logarithmic values of $\theta d^3/\nu^2$ and H/k are given.)

Source.	Diam. cm.	Temperature Excess (° C.).									
		30°.		100°.		200°.		600°.		1600°.	
		$\frac{\theta d^3}{\nu^2}$.	$\frac{H}{k}$.	$\frac{\theta d^3}{\nu^2}$.	$\frac{H}{k}$.	$\frac{\theta d^3}{\nu^2}$.	$\frac{H}{k}$.	$\frac{\theta d^3}{\nu^2}$.	$\frac{H}{k}$.	$\frac{\theta d^3}{\nu^2}$.	$\frac{H}{k}$.
B.........	0·0031	$\bar{5}$·55	0·14	$\bar{5}$·90	0·21	$\bar{5}$·98	0·32	...	...	...	...
A.........	0·00404	...	...	...	...	$\bar{4}$·32	0·25	$\bar{4}$·22	0·20	$\bar{5}$·74	0·24
B.........	0·0051	$\bar{4}$·20	0·22	$\bar{4}$·55	0·31	$\bar{4}$·63	0·31	...	...	...	...
A.........	0·00691	...	...	...	...	$\bar{3}$·02	0·29	$\bar{4}$·92	0·26	$\bar{4}$·44	0·29
B.........	0·0074	$\bar{4}$·69	$\bar{1}$·99	$\bar{3}$·04	0·24	$\bar{3}$·11	0·25	...	...	...	...
D.........	0·0114	...	...	$\bar{3}$·59	0·29	$\bar{3}$·67	0·29	...	...	...	...
A.........	0·01262	...	...	...	...	$\bar{3}$·80	0·32	$\bar{3}$·70	0·30	$\bar{3}$·23	0·29
B.........	0·0152	$\bar{3}$·62	0·30	$\bar{3}$·97	0·34	$\bar{2}$·05	0·36	...	...	...	...
A.........	0·02508	...	...	...	...	$\bar{2}$·70	0·44	$\bar{2}$·60	0·41	$\bar{2}$·12	0·34
B.........	0·0356	...	...	$\bar{1}$·08	0·53	$\bar{1}$·16	0·53	...	...	...	...
A.........	0·051	...	...	...	...	$\bar{1}$·62	0·55	$\bar{1}$·52	0·52	$\bar{1}$·05	0·49
D.........	0·0691	...	...	$\bar{1}$·94	0·58	0·02	0·58	...	...	...	...
E.........	0·1106	...	...	0·48	0·63	...	...	...	...	...	...
C.........	0·51	...	...	2·55	1·11	2·62	1·17	...	...	...	...
C.........	5·08	...	...	5·55	1·88	5·62	1·93	...	...	...	...
C.........	30·48	...	...	7·88	2·61	7·95	2·67	...	...	...	...
D *	0·0114	...	...	$\bar{3}$·00	0·26	$\bar{3}$·07	0·23	...	...	...	...
D ** ...	0·0114	...	...	$\bar{2}$·20	0·35	$\bar{2}$·27	0·35	...	...	...	...
D *	0·0691	...	...	$\bar{1}$·35	0·50	$\bar{1}$·42	0·51	...	...	...	...
D ** ...	0·0691	...	...	0·55	0·67	0·62	0·67	...	...	...	...

* Air at ½ atmosphere pressure. ** Air at 2 atmospheres pressure.

air with fine platinum wires at temperature excesses from 200° C. to 1600° C. He carefully corrected for radiation. His results may be represented to a certain degree of approximation by the formula $H \propto d^{1/5}\theta^{1/4}$, which does not agree with (3), where k and ν are regarded as constant; the disagreement is brought out even more clearly if θd^3 is plotted against H.

TABLE IV.

Convection Loss from Wire in Various Gases, at various pressures.

Wire diam. 0·1106 cm.

Source.	Gas.	Pressure Atm.	Temperature Excess (° C.).					
			100°.		300°.		900°.	
			$\frac{\theta d^3}{\nu^2}$.	$\frac{H}{k}$.	$\frac{\theta d^3}{\nu^2}$.	$\frac{H}{k}$.	$\frac{\theta d^3}{\nu^2}$.	$\frac{H}{k}$.
E.........	Air	0·1	$\bar{2}\cdot48$	0·40	$\bar{2}\cdot59$	0·45	$\bar{2}\cdot34$	0·53
		1·0	0·48	0·63	0·59	0·64	0·34	0·67
		10	2·48	0·95	2·59	0·97	2·34	0·99
		100	4·48	1·47	4·59	1·44	4·34	1·39
F.........	Hydrogen.	0·1	$\bar{4}\cdot82$	0·34	$\bar{4}\cdot91$	0·34	$\bar{4}\cdot69$	0·38
		1·0	$\bar{2}\cdot82$	0·38	$\bar{2}\cdot91$	0·40	$\bar{2}\cdot69$	0·44
		10	0·82	0·60	0·91	0·68	0·69	0·62
		100	2·82	1·00	2·91	1·03	2·69	0·99
G.........	Oxygen ...	0·1	$\bar{2}\cdot47$	0·40	$\bar{2}\cdot56$	0·44	$\bar{2}\cdot30$	0·57
		1·0	0·47	0·66	0·56	0·66	0·30	0·67
		10	2·47	0·93	2·56	0·95	2·30	0·96
		100	4·47	1·47	4·56	1·45	4·30	1·45

In fig. 1 all the Langmuir values of Table III. are plotted.

(B) Ayrton and Kilgour [*] worked with fine wires at more moderate temperature excesses. Table III. contains values for all their wires, but for convenience fig. 1 only shows values for the largest and the smallest. It should be mentioned that one wire (0·0074 cm. diam.) gives results at low temperature excess in poor agreement with the line in fig. 1. However, study of their curves shows that the behaviour of this particular wire is exceptional.

(C) Petavel [†] has given data for the total heat loss from the oxidized iron surface of steam pipes of various diameters up to 1 foot, a diameter which is ten thousand times the

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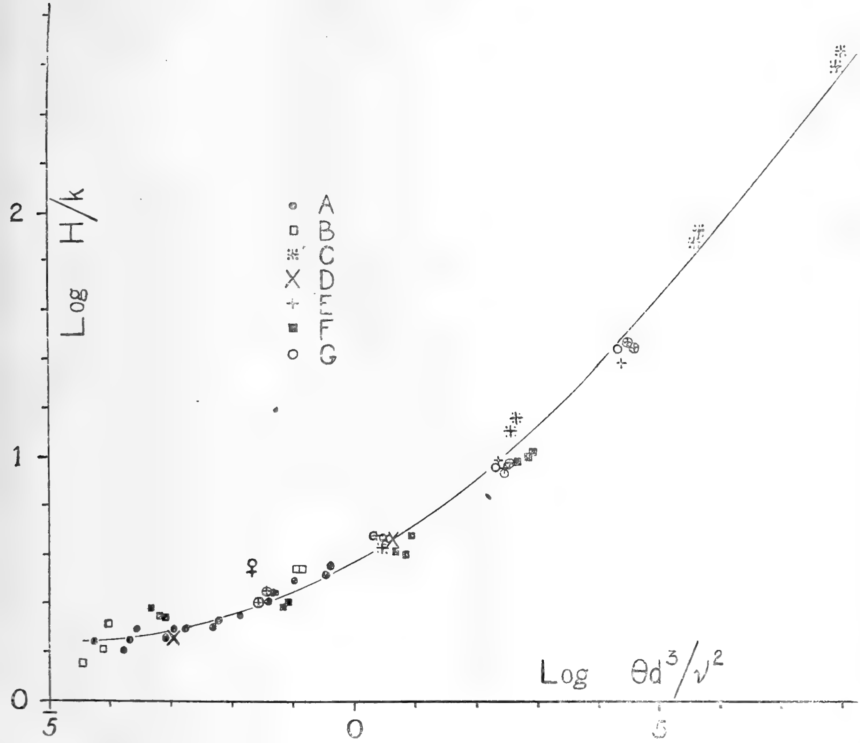
[*] Ayrton & Kilgour, Phil. Trans. A, clxxxiii. p. 371 (1892).

[†] Petavel, Proc. Manchester Assoc. Engineers, 1915–16.

diameter of Ayrton and Kilgour's smallest wire. Values with radiation eliminated are plotted in fig. 1.

(D) Kennelly * investigated the heat losses from wires in very large enclosures at various pressures, thus introducing another experimental variable.

Fig. 1.



Langmuir † has corrected these for radiation, and his corrected values have been used in compiling Table III. The points, if plotted on fig. 1, are in excellent agreement, but to preserve a clear figure only two points are shown, these corresponding to the extremities of the range.

(E, F, & G) Petavel ‡, who worked over a wide range of pressure (1/10 to 100 atm.) and up to 1100° C. excess, has given data by means of which the performance of different

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* Kennelly, Trans. A.I.E.E. xxviii. (1) p. 363 (1909).

† Langmuir, Trans. A.I.E.E. xxxi. (1) p. 1228 (1912).

‡ Petavel, Phil. Trans. A, cxcvii. p. 229 (1901).

gases may be compared. He studied the cooling of 0·1106 cm. wire, using a cylindrical water-cooled enclosure. Values have been plotted on the graph of fig. 1 instead of on a separate graph. The radiation correction is not large and in its calculation the enclosure temperature has been taken as 300° absolute. E, F, and G refer respectively to air, hydrogen, and oxygen. The point for the case of 1/10 atmosphere and 900° C. temperature excess is seen to lie rather high for each of the gases considered.

(5) *Conclusion.*

The curve of fig. 1 shows that very diverse data give points which, in general, all lie on one line independent of the size and temperature excess of the object, and of the nature and pressure of the gas involved. It therefore appears that the hydrodynamical theory of convection represented by our formulæ is substantially satisfactory even in the case of hot thin wires, provided allowance[*] is made for the temperature change of the properties of the fluid, an allowance brought into prominence by the high temperatures to which wires are usually heated in convection experiments. High temperatures are also used in experiments on *forced* convection from wires, and it is desirable to notice that in this case approximate agreement with the appropriate formula is found even without allowing for the temperature variations of the properties of the fluid, but that agreement is improved when such allowance is made[†].

Langmuir developed a theory of convection in which bodies are considered to be surrounded by a film of gas through which the heat is transmitted by pure conduction, and with certain assumptions, and allowing for the temperature change of the conductivity of the gas, he obtained results in agreement with experiment for free convection. However, he concludes that "for forced convection the film theory does not seem to apply"[‡].

It may be counted a superiority of the hydrodynamical theory that the treatment which reconciles theory with experiment for free convection is satisfactory for forced convection also.

Besides testing the hydrodynamical theory, fig. 1 effects a graphical correlation of diverse convection data for various gases and gas pressures over a wide range of wire diameter

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[*] Only approximate allowance is made in this paper.

[†] Davis, Phil. Mag. xli. p. 899 (1921).

[‡] Langmuir, Trans. Am. Electrochem. Soc. xxiii. p. 329 (1913).

and temperature excess. The tendency of the curve appears to be, at its upper extremity, towards the form

$$H/k \propto (\theta d^3/\nu^2) \quad , \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and at its other end towards

$$H/k = \text{constant.} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Equation (11) would imply that for large bodies the heat loss per unit *area* is independent of the size, and (12) that for very fine wires the heat loss per unit *length* is independent of the diameter. Equation (12) would also imply that the convective cooling of wires, very fine and very slightly heated, is a measure of the conductivity of the fluid, at any rate for fluids of such similar molecular constitution that $c\nu/k$ is the same.

May 1921.

XXXII. *The Frequency of the Electrons in the Neon Atom.*
By LAURENCE ST. C. BROUGHALL *.

MANY attempts have been made to arrange the electrons in the atoms of the inert gases, but it has been found that no stable arrangements can be obtained if only electrostatic forces are present. We are thus obliged to search for some other force, and the most reasonable assumption is that the electrons are in motion in circular orbits and so have an acceleration towards their axis of rotation. The main objection to this theory is that the electron since it rotates should radiate energy, and the diameter of its orbit should gradually diminish. Experimental evidence shows, however, that this is not the case, and so if we are to allow the electrons to rotate then we must assume that they radiate no energy. This assumption made by Bohr has met with great success in the case of hydrogen, where he assumes that the electrons radiate energy only when dropping suddenly into a different orbit. In consequence of this we have assumed throughout this paper that no energy is radiated by the electrons in the neon atom under normal conditions.

The number of electrons in the neon atom is ten, and Langmuir has shown that the most satisfactory arrangement of these ten electrons is to place eight of them at the corners of a cube and to place the other two within the cube. He

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* Communicated by the Author.

is led to this arrangement by a consideration of the valency of the elements, and also his hypothesis shows that the properties of neon should be similar to those of helium and argon.

There is also considerable evidence that the atom or molecule of neon is spherical, and the diameter of the atom has been calculated by two methods. It has been found by means of the viscosity of the gas, and secondly, W. L. Bragg has given a value for "d" the diameter of the atom of neon after consideration of the diameters of the atoms of elements which have atomic numbers near that of neon.

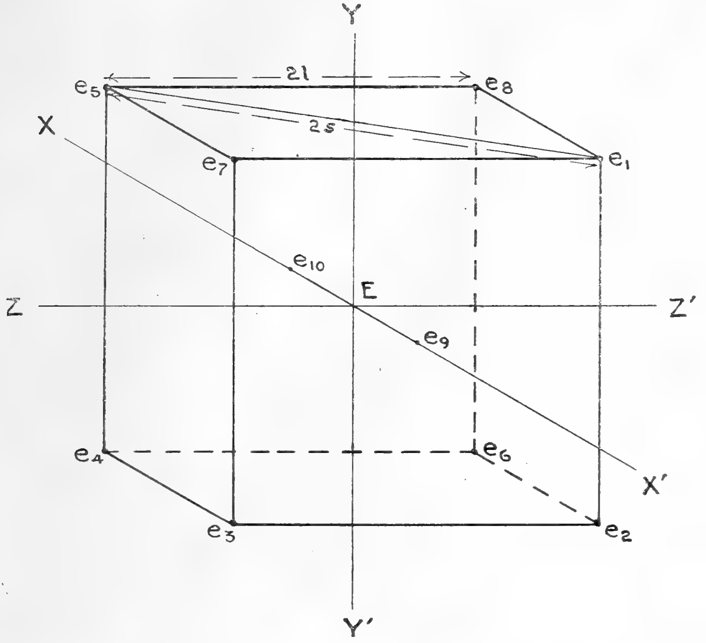
Representing the diameter found by viscosity measurement by "σ" we obtain the following values for neon: $\sigma=2{\cdot}35\times10^{-8}$, $d=1{\cdot}30\times10^{-8}$ cm. Now the value for "d" is very much less than the value for "σ" and it is supposed that when two molecules collide they do not come into contact. W. L. Bragg considers that his value for the atomic diameter is the distance between the outside electrons. In consequence of this we shall use the value $d=1{\cdot}30\times10^{-8}$ cm. for the real diameter of the neon atom.

In order to obtain a spherical atom by the rotation of eight electrons at the corners of a cube there are several possible axes of rotation, but the simplest case is to assume that the atom rotates about three perpendicular axes XX′, YY′, ZZ′. YY′ is determined by the mid points of the surfaces of any opposite pair of sides of the cube. In a similar manner XX′ and ZZ′ are determined by taking different pairs of sides. Using these axes of rotation the atom will have a radius equal to one half the diagonal of the cube, and this will be represented by "c." Further, for simplicity the lengths of the edges and of the surface diagonals will be represented by "$2l$" and "$2s$" respectively, since the representation of "l" and "s" as functions of "c" tends to make the work obscure.

We see that these axes of rotation give all the electrons in the outer shell or octet similar velocities, and it is for this reason of symmetry that these axes have been adopted in preference to all others.

The question now arises as to what will be the positions of the other two electrons. We desire if possible to make the forces acting on the other electrons the same for all of them, and the only possible positions for the electrons e_9 and e_{10} is to place them on one of the axes XX′, YY′, or ZZ′. It is quite immaterial which axis we take, but the electrons are assumed to be upon the axis XX′ throughout this paper, and are at a distance "r" cms. from the nucleus, which latter is at the centre of the atom. Since these two inner electrons are upon one of the axes of rotation, it follows that they only have two velocities, but this is sufficient to make the shell mapped out by these electrons spherical in shape.

Fig. 1.



The next point that arises is with regard to the laws of force holding between two electrons in the atom, and as there is no experimental evidence to the contrary we imagine that the inverse square law holds good.

We are now in a position to calculate the forces acting on any electron in the outer shell. We shall resolve the forces along the three perpendicular lines e_1e_8, e_1e_2, and e_1e_7. Since the electron is to be in equilibrium under the forces present, it follows that the total force acting along any one of the three perpendicular lines must be zero, and so we obtain three equations.

Let us first take the forces acting along the line e_1e_8, and further let the positive direction be $\overrightarrow{e_1e_8}$. The charge on the electron is "e." Charge of nucleus $=\mathrm{E}=10e$. Mass of electrons when moving with a small velocity $=m$. Angular velocity about YY$'=\omega_1$. Angular velocity about XX$'=\omega_3$. Angular velocity about ZZ$'=\omega_2$.

Using this notation we have :—

(1) Force due to $e_8=-\frac{e^2}{4l^2}$.

(2) Force due to e_6=force due to $e_5=-\frac{e^2}{4s^2}\cdot\frac{l}{s}$.

(3) Force due to $e_4=-\frac{e^2}{4c^2}\cdot\frac{l}{c}$.

(4) Force due to nucleus$=+\frac{10e^2}{c^2}\cdot\frac{l}{c}$.

(5) Force due to $e_{10}=-\frac{e^2}{(r+l)^2+s^2}\cdot\frac{r+l}{\sqrt{(r+l)^2+s^2}}$

$$=-\frac{e^2(r+l)}{[(r+l)^2+s^2]^{\frac{3}{2}}}.$$

(6) Force due to $e_9=+\frac{e^2}{(r-l)^2+s^2}\cdot\frac{r-l}{\sqrt{(r-l)^2+s^2}}$

$$=+\frac{e^2(r-l)}{[(r-l)^2+s^2]^{\frac{3}{2}}}.$$

(7) Forces due to e_7, e_3, and $e_2=0$.

(8) Force due to centrifugal force owing to rotation about axis YY$'=-\omega_1{}^2s\cdot\frac{l}{s}m=-\omega_1{}^2ml$.

(9) Centrifugal force due to rotation about axis ZZ$'$ $=-\omega_2{}^2s\cdot\frac{l}{s}m=-\omega_2{}^2ml$.

Since the sum of these forces must be zero, we obtain the equation

$$\text{(I.)}\quad \frac{39e^2}{4c^2}\cdot\frac{l}{c}=\frac{e^2}{4l^2}+\frac{e^2l}{2s^3}+\frac{e^2(r+l)}{[(r+l)^2+s^2]^{\frac{3}{2}}}-\frac{e^2(r-l)}{[(r-l)^2+s^2]^{\frac{3}{2}}}+m\omega_1{}^2l+m\omega_2{}^2l.$$

If we resolve along the line e_1e_7 and equate the total force to zero we obtain the equation

$$\text{(II.)}\quad \frac{39e^2}{4c^2}\cdot\frac{l}{c}=\frac{e^2}{4l^2}+\frac{e^2l}{2s^3}+\frac{e^2l}{[(r+l)^2+s^2]^{\frac{3}{2}}}+\frac{e^2l}{[(r-l)^2+s^2]^{\frac{3}{2}}}+m\omega_1{}^2l+m\omega_3{}^2l.$$

Similarly resolving along the line e_1e_2 we have

$$\text{(III.)}\quad \frac{39e^2}{4c^2}\cdot\frac{l}{c}=\frac{e^2}{4l^2}+\frac{e^2l}{2s^3}+\frac{e^2l}{[(r+l)^2+s^2]^{\frac{3}{2}}}+\frac{e^2l}{[(r-l)^2+s^2]^{\frac{3}{2}}}+m\omega_2^2l+m\omega_3^2l.$$

Subtracting equations (II.) from (III.) we have

$$m\omega_2^2l-m\omega_1^2l=0\,;$$

and therefore $\omega_1=\omega_2$.

Replacing "ω_2" by "ω_1" in equation (I.) we obtain

$$\text{(IV.)}\quad \frac{39e^2l}{4c^3}=\frac{e^2}{4l^2}+\frac{e^2l}{2s^3}+\frac{e^2(r+l)}{[(r+l)^2+s^2]^{\frac{3}{2}}}-\frac{e^2(r-l)}{[(r-l)^2+s^2]^{\frac{3}{2}}}+2m\omega_1^2l.$$

Another equation is required before we can find ω_1, ω_3, and "r." This equation can be found by finding the force acting on electron "e_9" along the line e_9e_{10}, and equating the total force to zero.

Performing this operation we have

$$\text{(V.)}\quad \frac{10e^2}{r^2}=\frac{4e^2(r+l)}{[(r+l)^2+s^2]^{\frac{3}{2}}}+\frac{4e^2(r-l)}{[(r-l)^2+s^2]^{\frac{3}{2}}}+\frac{e^2}{4r^2}+2m\omega_1^2r.$$

Which may be expressed in the form

$$\text{(VI.)}\quad 2m\omega_1^2l=\frac{39e^2l}{4r^3}-\frac{4e^2l(r+l)}{r[(r+l)^2+s^2]^{\frac{3}{2}}}-\frac{4e^2l(r-l)}{r[(r-l)^2+s^2]^{\frac{3}{2}}}.$$

Substituting this value for $2m\omega_1^2l$ in (IV.) and dividing throughout by "e^2" we obtain the equation

$$\text{(VII.)}\quad \frac{l}{4}\left\{\frac{39}{c^3}-\frac{1}{l^3}-\frac{2}{s^3}\right\}=\frac{r+l}{[(r+l)^2+s^2]^{\frac{3}{2}}}\left\{1-\frac{4l}{r}\right\}-\frac{r-l}{[(r-l)^2+s^2]^{\frac{3}{2}}}\left\{1+\frac{4l}{r}\right\}+\frac{39l}{4r^3}.$$

This equation contains no unknown quantity except "r." Now $c=6{\cdot}5\times10^{-9}$, $\therefore\ l=3{\cdot}75\times10^{-9}$ and $s=5{\cdot}31\times10^{-9}$. Putting these values for s, l, and c, we obtain the equation

$$\text{(VIII.)}\quad 1{\cdot}04\times10^{17}=\frac{r+3{\cdot}75\times10^{-9}}{[(r+3{\cdot}75\times10^{-9})^2+28{\cdot}2\times10^{-18}]^{\frac{3}{2}}}\times\left\{1-\frac{15\times10^{-9}}{r}\right\}-\frac{r-3{\cdot}75\times10^{-9}}{[(r-3{\cdot}75\times10^{-9})^2+28{\cdot}2\times10^{-18}]^{\frac{3}{2}}}\times\left\{1+\frac{15\times10^{-9}}{r}\right\}+\frac{36{\cdot}6\times10^{-9}}{r^3}.$$

Solving this equation in "r" we find that it is satisfied when $r=6{\cdot}1\times10^{-9}$ cm.

From equation (VI.) we may obtain an equation for ω_1:

$$\text{(IX.)} \quad \omega_1^2=\frac{e^2}{2rm}\left\{\frac{39}{4r^2}-\frac{4(r+l)}{[(r+l)^2+s^2]^{\frac{3}{2}}}-\frac{4(r-l)}{[(r-l)^2+s^2]^{\frac{3}{2}}}\right\}.$$

Putting $e=4{\cdot}774\times10^{-10}$ E.S.U. and $m=8{\cdot}8\times10^{-28}$ grm. we find that $\omega_1=6{\cdot}28\times10^{16}$ radians/sec.

Subtracting equation (II.) from equation (I.) we find that

$$\text{(X.)} \quad e^2r\left\{\frac{1}{[(r-l)^2+s^2]^{\frac{3}{2}}}-\frac{1}{[(r+l)^2+s^2]^{\frac{3}{2}}}\right\}=ml(\omega_1^2-\omega_3^2).$$

Substituting in this equation for e, r, l, s, m, and ω_1, we find that $\omega_3=4{\cdot}58\times10^{16}$ radians/sec.

From this we can now find the frequency about the axes ZZ′ and YY′ (n_1) and about the axis XX′ (n_3).

Also we may calculate the instantaneous linear velocities of the electrons in the outer or inner shells. Taking the case of the outer shell we determine the linear velocity due to rotation about ZZ′ or YY′ (v_1) and due to rotation about XX′ (v_3).

Tabulating the results we find that:—

Frequency of the electrons about XX′
$=n_3=\cdot73\times10^{16}$.

Frequency of the electrons about YY′ and ZZ′
$=n_1=1{\cdot}00\times10^{16}$.

Angular velocity of the electrons about XX′
$=\omega_3=4{\cdot}58\times10^{16}$rad./sec.

Angular velocity of the electrons about YY′ and ZZ′
$=\omega_1=6{\cdot}28\times10^{16}$ rad./sec.

Instantaneous linear velocity of the outer electrons
about XX′$=v_3=$ $2{\cdot}98\times10^8$ cms./sec.

Instantaneous linear velocity of the outer electrons
about YY′ and ZZ′$=v_1=4{\cdot}08\times10^8$ cms./sec.

Instantaneous linear velocity of the inner electrons
about YY′ and ZZ′$=3{\cdot}83\times10^8$ cms./sec.

The value of "v" will be seen to be small compared with the velocity of light, in consequence of which it follows that we have committed no appreciable error in not correcting for the variation of mass with velocity according to the equation $m_v=m_0(1-v^2/c^2)^{\frac{1}{2}}$ where "c" is the velocity of light.

October 15, 1921

XXXIII. *An Attempt to determine whether a Minimum Time is necessary to excite the Human Retina. By* J. H. J. POOLE, *Sc.D.**

IN a letter to 'Nature,' published on April 7th, 1921, Sir Oliver Lodge suggested that possibly there might be a certain minimum time necessary for a beam of light to liberate an electron from a photo-electric surface. Thus, assuming that the area of wave-front which can contribute energy to a very small resonator, like the electron, is of the order of λ^2/π, he showed that for ordinary sunlight the surface would have to be illuminated for about $\frac{1}{1000}$ sec. before an electron could be liberated. It seems, however, improbable that such a comparatively large interval of time should be necessary to excite an electron, especially as photographs, in which the action of the light on the sensitive film is probably due to the liberation of such electrons, can be taken in ordinary sunlight with exposures shorter than this.

As a matter of fact, at the time that Sir Oliver Lodge published the above suggestion in 'Nature,' Dr. Joly and I had already undertaken some experiments with the view to seeing if any such effect held for the human retina. The general principle of the method is described by Dr. Joly in a letter to 'Nature' for April 14th, 1921, but perhaps a recapitulation of it is desirable.

The general idea of the method was to cause a parallel beam of light to revolve very rapidly by reflecting it from the surface of a rotating mirror. The revolving beam was then viewed through a narrow slit placed at a considerable distance from the mirror; and it is obvious that if the slit and the light-beam can both be kept narrow, then the resulting flash, seen by the eye, may be made very short indeed by running the mirror at a high speed, and also by making the distance between the mirror and the slit large.

In order to get as high a speed of rotation of the mirror as possible, it was mounted on the top of the vertical spindle of a Legendre Centrifuge. This centrifuge was capable of speeds up to about 8000 r.p.m., as was determined with a revolution counter and stop-watch. The mirror itself was a small speculum metal one, of about 4 cms. diameter, manufactured and ground optically plane by Sir Howard Grubb. During the course of the experiments this mirror

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* Communicated by Prof. J. Joly, F.R.S.

was re-polished by Hilger Ltd., as it was found that there was rather an undue amount of irregular reflexion taking place at the surface of the mirror. To avoid, as far as possible, any stray light from the mounting of the mirror or from its back reaching the eye, they were both carefully blackened by means of a small turpentine flame, which gave a very good deposit of lamp-black.

The chief difficulty experienced was with the optical arrangements. It is plain that it is impossible to realize the ideal of a perfectly parallel beam owing to the finite size of the light-radiant. The best we can do is to use as small a radiant as possible, and also as long a focus lens as we can without reducing the illumination too much. In the preliminary experiments a slit was used as the radiant, the light from a projection type of electric glow lamp being concentrated on it with a condensing lens. Between this slit and the mirror a long focus lens was placed, and the distance of the lens and the slit was so adjusted that the image of the latter was formed on the second slit behind which the eye was placed. The lens is naturally placed as close to the revolving mirror as possible, as the image formed will be magnified in the ratio of its distances from the two slits, while the speed of the image will be proportional to the distance of the mirror from what we might perhaps call the eye-slit ; thus the distance between the lens and the mirror only tends to enlarge the image without increasing the speed, and should hence be kept as small as is convenient. In the first trials this lens was of about 2 metres focal length, which was hardly sufficient. These experiments were conducted in an ordinary room, and it was found impossible to keep it sufficiently dark for the eye of the observer to become truly dark-adapted. The distance between the mirror and the eye-slit could only be made about 15 metres, a distance which it was thought could be increased with advantage.

On both these accounts it was decided to remove the apparatus to the cellars of this building. These cellars were particularly suitable for the purpose, as a distance of 30 metres could easily be obtained between the mirror and the eye-slit, and no trouble was experienced in keeping them nearly perfectly dark. Some modifications were also introduced into the arrangements as a result of our previous trials. Thus we had already found that even at the maximum speed of the centrifuge the light was plainly visible in the mirror. This showed that a flash of the order of about 10^{-6} sec. or rather less was visible if repeated sufficiently often. To be able to deal with one flash of this duration, however, it is necessary to use some method of only illuminating the mirror at intervals for less than a complete revolution, thus ensuring that only one flash reached the eye for each light interval. This end was brought about by interposing a revolving disk, with a sector of suitable size cut out, between the lens and the radiant. The dimensions of the sector removed from the disk were arranged so that when the disk was running at about 120 r.p.m. the length of flash should be about $\frac{1}{150}$ sec., which would be less than one revolution of the centrifuge. The frequency of the flashes seen by the observer in this case was about two per second. To drive the disk, it was mounted directly on the shaft of a variable speed repulsion motor. As a matter of fact, in practice the disk was driven at a slightly greater speed than 120 r.p.m. This increased the frequency of the flashes slightly, but diminished the chance of any light from two successive revolutions of the mirror reaching the eye.

The optical arrangements were also improved. New lenses of various focal lengths were obtained from Adam Hilger & Co. Finally a lens of about 4 metres focal length was found to answer most satisfactorily. If a longer focal length than this is used, the question of obtaining sufficient illumination in the beam becomes rather troublesome. Different forms of radiant were also tried. The plan of using a slit as radiant was abandoned as sufficient light could not be obtained from it. After trying various other light sources, a small galvanometer electric lamp supplied by the Cambridge & Paul Scientific Instrument Co. was found to work most satisfactorily. This lamp had a single loop filament, and by turning this loop parallel to the direction of the light-beam, a very fair approximation to a line source of light could be obtained.

The method of observing the flashes was as follows. One observer took up his position at the eye-slit, which was fitted with a small tube so that the direction of vision might be preserved constant in the dark. The other observer then started the centrifuge and ran it up to the required speed. In the meanwhile the revolving sector shutter was kept permanently open, so that what the first observer perceived was a steady light in the mirror. When he had satisfied himself that this light was visible, *i.e.* that the direction of the light-beam was correct, he gave a signal, and the sector shutter was started. This shutter was not, however, run continuously, but it was stopped in the open position occasionally, so that the observer might satisfy himself that the light-beam was reaching his eye correctly. This precaution is very necessary, owing to the fact that between the very feeble flashes that are visible when the revolving shutter is running, there is a great tendency for the direction of the eye to alter, as in the dark intervals there is nothing to fix its position very exactly.

It is also very necessary that the dark adaptation of the eye should be nearly perfect. For this purpose the observer should be at least twenty minutes in the dark before attempting to make any trials. The difference in sensitivity between ordinary daylight vision and fully dark-adapted vision is very large. Selig Hecht, in a paper published in the 'General Journal of Physiology' for May 1920, states that the dark-adapted eye is easily from 5,000 to 10,000 times more sensitive. To attain the maximum sensitivity it is necessary to be at least 45 minutes in the dark, but after 25 minutes the increase in sensitivity is very slow, hence probably the period of 20 minutes adopted in these experiments was sufficient to ensure that the eye would be nearly fully dark-adapted.

As regards the results obtained with this apparatus, it was found that a flash of 2×10^{-7} sec. was still visible. A flash of duration 8×10^{-8} sec. was, however, found to be invisible. This flash was, however, found to be visible if viewed directly without a slit, in which case the time of flash would be about $2{\cdot}4 \times 10^{-7}$ sec., thus confirming the previous result. The energy in each of these flashes could be approximately calculated from the candle-power of the radiant and the various dimensions of the apparatus, and it was found that, neglecting any loss by reflexion, etc., the energy in the visible flash was about 4×10^{-7} erg, while that in the invisible flash was about 8×10^{-8} erg. As to whether the invisibility of the shorter flash is due to its smaller duration alone or simply to the decrease in the energy available, is uncertain. It seems, however, that the latter hypothesis is more probable as the intensity of the longer flash was excessively feeble. The problem of getting more light into a flash of this nature is not very easy, as the amount of light which can be obtained depends only on the brightness of the radiant, and it is not very easy to get a suitable one which would be brighter than an electric light filament. An arc lamp might have given more light, but would not have been so convenient as a slit, and a condensing lens would have been required. Probably the increase in brightness would also not have been very large.

Iveagh Geological Laboratory,
Sept. 1921.

XXXIV. *The Analysis of Sound Waves by the Cochlea.* By H. E. Roaf. (*From the Department of Physiology, London Hospital Medical College.*)[*]

THE variations of air pressure which produce the sensation of sound are conveyed to the *fenestra ovalis* through the foot plate of the stapes. The mechanics of this conveyance is well described by Wrightson, who points out that the liquid in the internal ear is practically incompressible, therefore movements of the stapes can take place only by mass movements of liquid and by yielding of the membrane closing the *fenestra rotunda* [†].

Mass movement of the liquid can take place in one of two ways. Liquid may pass up the *scala vestibuli* through the *helicotrema* and down the *scala tympani*, or the *scala media* may be pushed towards the *scala tympani*. The resistance to these movements is in the former case the inertia of the mass of liquid to be moved, and the friction of the liquid against the walls of its containing tube, and in the latter case the tension of the basilar membrane (Reissner's membrane is usually represented as being flaccid). The relations of these two movements are shown in figs. 1 and 2. Fig. 1 represents the cochlea uncoiled, and arrows indicate the direction of movement of liquid if it were to take place through the *helicotrema*. Fig. 2 represents a cross section through one part of the coiled tube, and an arrow indicates movement of liquid when the basilar membrane is pushed towards the *scala tympani*.

The relation of movement of liquid along the *scalæ* to deformation of the basilar membrane is difficult to assess because the viscosity of the liquid and the tension of the basilar membrane are unknown, but the following factors are in operation. The resistance to movement is high in such small tubes as it is inversely proportional to the fourth power of the radius in circular tubes, and the shape of the *scalæ* is such that there is a relatively larger surface to area than if they were circular tubes. Such high resistance will damp any movement, so that the movements of the liquid will be "dead beat," such as are those associated with the recognition of tone [‡]. The width of the basilar membrane is greater the further up the cochlea it is measured, therefore it will be

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[*] Communicated by the Author.

[†] Sir Thomas Wrightson, 'The Analytical Mechanism of the Internal Ear,' Macmillan & Co. (1918).

[‡] H. Hartridge, J. Physiol. vol. liv. Proc. p. vii (1920).

deformed by less force, and at the same time there is a larger area for any pressure to act upon it. Thus the distal end of the cochlea will be moved by a lower pressure than will affect the proximal end.

Fig. 1.

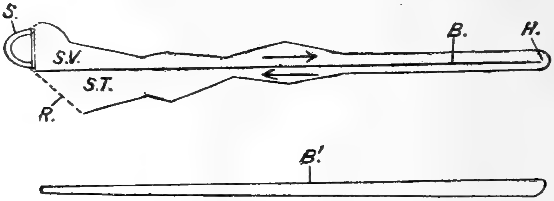

Diagram to show variations in area of the cochlear tubes and basilar membrane. The cochlea is represented as uncoiled. From Sir Arthur Keith, appendix to 'The Analytical Mechanism of the Internal Ear.'

Fig. 2.

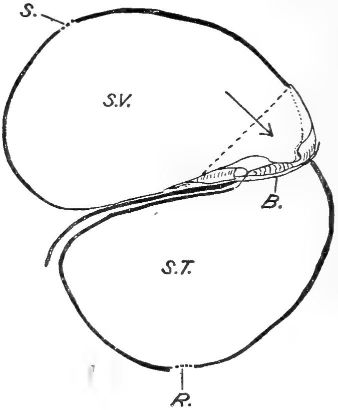

Diagram to show cross section of cochlear tube, the connexion of the *scala vestibuli* and *scala tympani* with the stapes and *fenestra rotunda* respectively are indicated by a break in the wall closed by a dotted line. From Sir Arthur Keith, appendix to 'The Analytical Mechanism of the Internal Ear.'

S.V.=*scala vestibuli*; S.T.=*scala tympani*; S.=*stapes*; R.=*fenestra rotunda*; H.=*helicotrema*; B.=basilar membrane. B'.=surface view of basilar membrane.

The mechanical conditions on which movement of the organ of Corti depend are practically unknown. If the basilar membrane consists merely of stretched strings and the rods of Corti behave as hinged structures, the force required to produce a definite movement in either direction will be inversely proportional to the length of fibre extended, *i. e.*, Young's modulus, or

$$\frac{\text{stretching force per unit area}}{\text{extension per unit length for circular fibres}} = \mathrm{FL}/\pi r^2 l.$$

If, on the other hand, the organ of Corti (including the rods of Corti and the tectorial membrane) acts as a rigid structure, the problem is similar to that of the bending of a bar, and the force required to produce the same amount of movement will be inversely proportional to the cube of the length of the structure, *i. e.*, Young's modulus $= 4\mathrm{FL}^3/bd^3l$. The mathematical treatment of this problem is not possible because we do not know the nature of the unions nor the physical properties of the structures concerned, but it is possible that the variation in ease of deformation may be much greater than is to be expected from the relative widths of the various portions of the basilar membrane. The problem is further complicated by the fact that the pectinate portion of the basilar membrane must also be stretched, even if the organ of Corti acts as a rigid bar.

Thus we see that rapid variations in pressure will not be able to set a long column of liquid in motion, but the *fenestra rotunda* being at atmospheric pressure there will be greater differences of pressure across the lower end of the basilar membrane, with the result that the proximal end of the basilar membrane will be deformed, thus stimulating the hair cells at the proximal end of the cochlea.

Slower variations in pressure will cause movement along the *scalæ* without producing sufficient difference in pressure to deform the proximal end of the basilar membrane. Somewhere along the basilar membrane the lower difference in pressure will be sufficient to deform the basilar membrane, with the result that the hair cells in that region will be stimulated.

Accordingly, it is evident that the impedance due to the mass and friction of the perilymph will tend to produce greater differences of pressure at the narrower end of the basilar membrane with rapid changes, whilst slower changes will cause lesser differences, so that the basilar membrane will be moved at a wider part.

Irregularities in the area of the *scalæ* will cause the impedance to vary, so that certain ranges of frequencies will be more accurately analysed than others.

It must be pointed out that other factors, such as the mass of the organ of Corti, will aid the analysis of the pressure variations.

The factor that is analysed is acceleration, which is proportional to the second differential coefficient of pressure in relation to time. The pressure-time relation is a sine curve, therefore $\frac{d^2x}{dt^2} = -\sin X$.

It must be remembered that a tone depends not on a single rise of pressure but on a succession of pressures, so that continuous movement occurs only at the part of the basilar membrane where the inertia and friction produce sufficient pressure to deform the basilar membrane.

The hypothesis of M. Meyer * does not treat the subject from the same physical standpoint as that described herein, because his hypothesis is based on the amplitude of the wave and not its frequency, nor do other hypotheses such as those of E. ter Kuile † and of Hurst ‡ explain analysis on the same basis.

It is assumed that the number of nerve-fibres and end organs are sufficient to account for the various frequencies distinguishable by the ear.

The mechanical conditions described above do not depend upon the presence of an organ of Corti, but the problem of tone analysis in birds requires further investigation. The exact anatomical arrangement of the cochlea and the range of tone analysis must be compared.

In order to show that a mechanism such as that described can analyse complex pressure waves, several models have been made of which the simplest for purposes of demonstration is that shown in fig. 3.

A glass U tube was made with a narrowed portion in the connecting limb to damp the oscillations, and several smaller tubes were blown on one limb of the U. The open ends of the side tubes are closed by glass bulbs of different sizes to represent the different elasticities of the parts of the basilar membrane. The apparatus is filled with water and a rubber bulb is fastened to the U tube at A: pressure variations are made by squeezing A.

With such a large scale apparatus it is not to be expected that it will respond to such rapid pressure variations as most sound waves, but it will respond to slower variations. For

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* M. Meyer, *Arch. f. d. ges. Physiol.* vol. lxxviii. p. 346 (1899) and vol. lxxxi. p. 61 (1900).

† E. ter Kuile, *Arch. f. d. ges. Physiol.* vol. lxxix. p. 146 (1900).

‡ C. H. Hurst, Trans. L'pool. Biol. Soc. vol. ix. p. 321 (1895).

instance, if one squeezes A gently and slowly there is a movement of liquid in the far limb of the U and also rapid oscillations in the tube nearest to A. These rapid oscillations are due to irregularities in the muscular contraction,

Fig. 3.

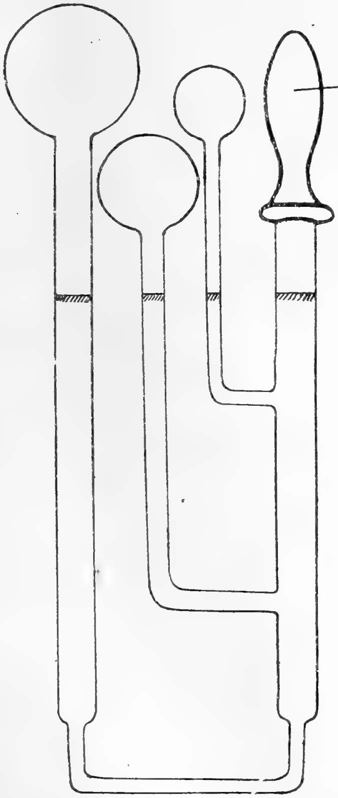

Diagram of apparatus for the analysis of pressure waves.
A = rubber bulb for producing pressure variations.

and with a proper apparatus it should be possible to show the individual contractions of which the complete movement is composed. In fact a similar apparatus is being used to analyse various sorts of tremors in patients.

Models more like the cochlea have been made, but they are not so convenient for purposes of demonstration.

Summary.

The factors of inertia of fluid and friction of perilymph against the walls of the *scalæ*, with the variation in elastic tension of the basilar membrane and organ of Corti, must have considerable influence in analysing complex pressure variations, and such factors are capable by themselves of analysing coarser pressure variations such as the irregular contractions constituting a slow muscular movement.

This process of analysis would satisfactorily account for summation and difference tones.

XXXV. *Notes on the Measurement of Absolute Viscosity.*
By FRANK M. LIDSTONE *.

IT appears to have generally escaped notice, that in any form of absolute viscometer where a variable head obtains, it is not strictly accurate to use the mean head when computing the viscosity.

When the difference between the initial and final heads is at all large as compared with the mean head, the error introduced becomes far from negligible.

If we take the general formula of Poiseuille,

$$\eta = \frac{\mathrm{K}th}{\mathrm{V}} \quad \text{or} \quad t = \frac{\eta \mathrm{V}}{\mathrm{K}h}.$$

Here h stands for the head, V for the volume, and t for the time of efflux. K represents the remainder of the constants, with which we are not at present concerned.

By taking all the heads, from the initial to the final, summing the times, and integrating the expression we get

$$\Sigma t = t = \frac{\eta \mathrm{V}}{\mathrm{K(H-F)}} \int_{\mathrm{F}}^{\mathrm{H}} \frac{dx}{x},$$

where H is the initial and F the final head. This gives us in place of the original equation

$$\eta = \frac{\mathrm{K}t(\mathrm{H-F})}{\mathrm{V}\log_e \frac{\mathrm{H}}{\mathrm{F}}}.$$

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* Communicated by the Author.

The factor $\frac{\mathrm{H-F}}{\log \mathrm{H/F}}$ rapidly approaches the mean head $\frac{1}{2}(\mathrm{H+F})$ as the initial and final heads become large as compared with their difference ; and as long as this fact is not lost sight of, there is no reason why the more cumbersome calculation should be necessary. The subjoined table shows at a glance the extent of the error involved.

Ratio of mean head to difference in heads.	Ratio of initial to final head.	Ratio of mean head to corrected head.	Percent. error.
$\frac{\frac{1}{2}(\mathrm{H+F})}{\mathrm{H-F}}$	$\frac{\mathrm{H}}{\mathrm{F}}$	$\frac{1}{2}(\mathrm{H+F}) \Big/ \frac{\mathrm{H-F}}{\log_e \frac{\mathrm{H}}{\mathrm{F}}}$	
n	$\frac{2n+1}{2n-1}$	$n \log_e \frac{2n+1}{2n-1}$	$100\left(n \log_e \frac{2n+1}{2n-1} - 1\right)$
$\frac{1}{2}$	∞	∞	∞
$\frac{5}{8}$	9	1·3733	37·33
$\frac{3}{4}$	5	1·2071	20·71
$\frac{7}{8}$	$3\frac{2}{3}$	1·1369	13·69
1	3	1·0986	9·86
$1\frac{1}{2}$	2	1·0397	3·97
2	$\frac{5}{3}$	1·0186	1·86
3	$\frac{7}{5}$	1·0094	0·94
4	$\frac{9}{7}$	1·0052	0·52
10	$\frac{21}{19}$	1·0008	0·08
20	$\frac{41}{39}$	1·0002	0·02
30	$\frac{61}{59}$	1·00015	0·015

The formulæ which have been advanced to correct for the kinetic energy of the liquid are almost as numerous as the factors they contain.

It might, therefore, be not out of place to work it out once again from first principles.

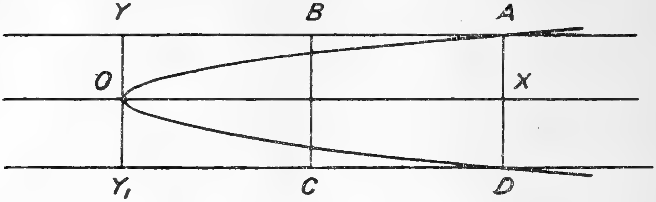
If W is taken as the total work done in the system, and $\mathrm{W_K}$ as that expended on kinetic energy, then we can write

$$\eta = \eta\,(\text{found}) \times \left(1 - \frac{\mathrm{W_K}}{\mathrm{W}}\right).$$

The total work W is equal to $\mathrm{V}\,.\,d\,.\,g\,.\,\frac{1}{2}(\mathrm{H+F})$, where V is the volume which passes any fixed point in the system ; d the density ; H the initial, and F the final head.

The allowance to be made for the work expended on kinetic energy is rather more elusive than it appears at first sight.

Let AYY_1D represent a section of the capillary and ABCD the volume which passes in unit time. Then if AY is made equal to 2 AB the paraboloid of revolution AOD (which is equal in volume to ABCD) represents the actual flow of the liquid which passes in unit time.



Then if $OX=h$ and radius $OY=r$, we have: apparent kinetic energy of volume AYY_1D is equal to

$$\frac{\pi r^2 dh^3}{8} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . (1)$$

Actual kinetic energy of volume AYY_1D at any instant of time *in* the tube is equal to

$$\frac{\pi r^2 d}{64a^3}\int_0^r y(r^2-y^2)^2 dy = \frac{\pi r^2 dh^3}{6} \quad . \quad . \quad . \quad . \quad (2)$$

Kinetic energy of volume *equal* to AYY_1D which *leaves* the tube, is twice the kinetic energy possessed by the volume AOD, namely,

$$2\times\frac{\pi d}{64a^3}\int_0^r y(r^2-y^2)^3 dy = \frac{\pi r^2 dh^3}{4} \quad . \quad . \quad . \quad (3)$$

The value of (3) is exactly double that of (1). Hence if a liquid flows through a eapillary with a mean velocity of v, the work done in giving it its kinetic energy is $2\times\frac{1}{2}mv^2$ if m is the mass which has left the tube.

If then we take this value and integrate between the initial and final heads, H and F respectively, we get for the total work expended on kinetic energy,

$$W_K = \frac{4Vdv^2}{(H-F)(H+F)^2}\int_F^H x^2 dx$$

$$= \tfrac{4}{3}Vdv^2\left(1-\frac{HF}{(H+F)^2}\right),$$

and

$$\frac{W_K}{W} = \frac{8v^2\left\{1-\frac{HF}{(H+F)^2}\right\}}{3g(H+F)}.$$

The amended equation of Poiseuille thus becomes

$$\eta=\frac{\pi r^4 g d t\,(\mathrm{H}-\mathrm{F})}{8\mathrm{V}a\log_e\frac{\mathrm{H}}{\mathrm{F}}}\left\{1-\frac{8v^2\left(1-\frac{\mathrm{HF}}{(\mathrm{H}+\mathrm{F})^2}\right)}{3g(\mathrm{H}+\mathrm{F})}\right\}.$$

The apparent mean velocity v being equal to $\frac{\mathrm{V}}{\pi r^2 t}$ it becomes more convenient for purposes of calculation to write it thus:

$$\eta=\frac{\pi r^4 g d t(\mathrm{H}-\mathrm{F})}{8\mathrm{V}a\log_e\frac{\mathrm{H}}{\mathrm{F}}}-\frac{\mathrm{V}d(\mathrm{H}^3-\mathrm{F}^3)}{3\pi a t(\mathrm{H}+\mathrm{F})^3\log_e\frac{\mathrm{H}}{\mathrm{F}}}.$$

XXXVI. *On the Phenomenon of the "Radiant Spectrum" observed by Sir David Brewster. By* C. V. Raman, *M.A., Palit Professor of Physics in the Calcutta University* *.

In a paper on "The Scattering of Light in the Refractive Media of the Eye," published in the Philosophical Magazine for November 1919 (p. 568), I discussed the explanation of the luminous effects observed when a small brilliant source of light is viewed directly by the eye against a dark background, and especially of the marked difference between the cases in which the source emits white light and highly monochromatic light respectively. In both cases the source appears to be surrounded by a diffraction-halo; but the structure of the halo is markedly different in appearance. In the former case, the source appears to shoot out streamers of light radiating from it in all directions, these streamers showing marked colour, and in fact appearing as elongated spectra in the outer parts of the halo. With the monochromatic light-source, on the other hand, the radiant structure of the halo is not observed, and we have instead surrounding the light-source a halo showing dark and bright rings and exhibiting a finely mottled or granular appearance. It was pointed out in the paper that these effects are precisely what might be expected on the hypothesis that the halo seen surrounding the source is due to the diffraction of light by a large number of particles of constant size—presumably the corneal corpuscles—present in the refractive media of the eye. The radiant structure of the halo in

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* Communicated by the Author. Read before the Royal Society of Edinburgh, Nov. 7, 1921.

white light and its granular structure in highly monochromatic light is, on this view, due to the field of light diffracted by individual particles varying arbitrarily in intensity from point to point as the result of the mutual interference of the effects of the large number of such particles. A closely analogous structure of the luminous field may be observed in diffraction-haloes obtained in other ways, *e. g.* with the aid of a glass plate dusted with lycopodium powder through which a small distant source of light is viewed.

The facts mentioned above provide a very simple explanation of a remarkable observation made long ago by Sir David Brewster, and communicated to the Royal Society of Edinburgh (Proceedings, vi. p. 147 * ; see also Phil. Mag. September 1867), which has not up to now been satisfactorily accounted for, and to which my attention has been recently drawn by Dr. C. G. Knott while I was on a visit to Edinburgh. Brewster noticed that when a spectrum of a small brilliant source of white light is formed, either by a prism or by diffraction, and viewed directly by the eye, a patch of light is seen lying in the continuation of the spectrum well beyond its violet end and exhibiting streamers radiating from its centre. That this is a diffraction-effect is shown by the fact that a similar and even more striking effect may be observed in the diffraction-halo due to a glass plate dusted with lycopodium held together with a 60° glass prism before the eye, when a small distant source of white light is viewed through the combination. The prism disperses the image of the source into a spectrum. It also disperses the diffraction-halo, and since the diffraction-rings are of different size for the different wave-lengths and are shifted to different extents owing to the dispersive power of the prism, the achromatic centre of the halo is shifted laterally to a considerable extent, its new position generally lying at a point much removed beyond the violet end of the spectrum of the source itself. The elongated spectra which form the radiating streamers are rotated through various angles by the dispersion of the prism, being drawn out laterally on one side and shut up or drawn together on the other side, and they then appear to diverge from the shifted position of the achromatic centre of the halo, which, as remarked above, now lies well beyond the violet end of the spectrum of the source. The analogy between this effect and Brewster's phenomenon is so striking that there can be no doubt that the latter is essentially of the same nature, the diffraction in this case being due to the structures within the eye itself.

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* See also a brief note by Tait, Proc. R. S. E. vi. p. 167.

XXXVII. *On the Form of the Temperature Wave spreading by Conduction from Point and Spherical Sources; with a suggested application to the Problem of Spark Ignition.*

By E. TAYLOR JONES, *D.Sc., Professor of Physics in the University College of North Wales,* J. D. MORGAN, *B.Sc., and* R. V. WHEELER, *D.Sc., Professor of Fuel Technology in the University of Sheffield**.

IT is natural to assume that the power of igniting inflammable gaseous mixtures possessed by an electric spark depends essentially upon its ability to impart heat to the gaseous mixture, and that in this respect it behaves similarly to any other source of heat. Most, if not all, investigators of the phenomena of the ignition of gases by electric sparks have entered upon their work with this assumption. An obvious inference is that the heat just necessary to ignite a given mixture under standard conditions should be a constant quantity, and that the heat contents of all sparks that are just capable of igniting such a mixture, no matter how those sparks are produced, should be the same.

It has, however, been definitely established by experiment that the thermal energy of a spark that is just capable of igniting a given mixture varies considerably with the electrical conditions under which the spark is produced. This has led to the view that electric-spark ignition is not mainly, if at all, a thermal process; that it is, in fact, mainly due to ionization.

Inasmuch as the rate of reaction between oxygen and inflammable gas is increased if the mixture is ionized, and the attainment of the ignition temperature of a gaseous mixture is mainly dependent upon this rate of reaction, it can readily be understood that means of ignition that perform the dual function of ionizing a mixture and imparting heat to it (either successively or concurrently) may be more effective than those which only impart heat, if such there be.

The common means of ignition of gaseous mixtures—heated wires or surfaces, or jets of flame—are powerful sources of ionization, though they are usually supposed to cause ignition by virtue of the heat they supply. The debateable question would therefore appear to be: Are electric sparks so much more potent sources of ionization than, say, heated surfaces as to warrant the process of ignition of gaseous mixtures by the former being labelled "ionic" in contradistinction to a "thermal" process of ignition by the latter? Or, assuming that there are marked differences

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* Communicated by the Authors.

between the ionizing powers possessed by various igniting agents (or by various types of electric sparks), do these differences effect changes in the rationale of ignition of a given series of inflammable mixtures?

The object of the present paper is to show that, given gaseous mixtures or series of mixtures of constant composition, a variation in the energy of the electric spark required to ignite them, dependent on the character of the spark, is to be anticipated on thermal considerations alone.

The ignition of a gaseous mixture depends primarily on the attainment of a sufficiently rapid rate of reaction within a sufficient mass, or, expressed on a thermal basis, on the heating of a sufficient volume to a sufficient temperature.

If whilst the requisite volume of a given mixture was being raised to the required temperature it could be isolated, so that no heat could escape to the surrounding gas, then (presuming that no complicating effect were introduced by the mode of imparting the heat) it might reasonably be expected that the quantity of heat required to ignite that mixture would be constant. An unavoidable condition in practice, however, is that whilst that portion of the mixture adjacent to the source of ignition is receiving heat, it is also communicating heat to the surrounding gas. The distribution of temperature at any instant throughout the volume of the mixture will vary with the character of the source, even though the total quantity of heat delivered by each source may be the same.

A starting-point in an examination of the manner in which thermal energy is conveyed to a gaseous mixture by an electric spark, is given by an inquiry into the manner in which the distribution of temperature varies with time when a source of heat corresponding in general character with a spark is introduced into a gas. Electric sparks can be divided into two main classes: (i.) those of exceedingly short duration (such as single capacity sparks), and (ii.) those of relatively long duration (such as inductance sparks). It will be advantageous, therefore, to consider the thermal distribution in a gas afforded by hypothetical sources of heat of (i.) instantaneous, and (ii.) continued character. In order, also, to obtain some idea of the effect of the volume of an electric spark on its igniting power, or "incendivity," point and spherical sources of heat will be considered.

The subject is here treated mainly as a problem in thermal conduction in a uniform medium, and, to avoid complication, the medium chosen is air. The numerical results obtained may not represent at all closely the manner in which heat actually spreads from a spark in an inflammable mixture. In a full treatment of the problem, the effect of the pressure-wave emanating from the spark, and the effects of convection, radiation, conduction through the electrodes, and variable conductivity of the medium must be taken into account. Above all, the fact that during the process of ignition chemical combination is proceeding causes the temperature wave to be more elevated than it would be as a result of a purely physical transmission of heat. The general effect of the heat added to the system by chemical action would be to intensify those differences that are shown to arise from purely physical causes between one type of source of heat and another. A temperature wave-form in which a considerable volume of gas is raised by conduction of heat to the temperature required for active combination to take place, would be accompanied by a greater supply of "chemical heat" than one in which the region of high temperature is more restricted; the chemical heat would therefore more greatly enhance the effect of the source in the former than in the latter instance.

Our immediate purpose being to inquire what influence, if any, the manner of supply of heat to the medium has upon the wave-form, we will suppose that the total quantity of heat (Q) supplied is constant. This quantity we will assume to be supplied to the medium either at a point or throughout a space symmetrically surrounding a point which is taken as origin. Under these circumstances the temperature, θ, at any point in the medium at a distance, r, from the origin, and at a time, t, after heating begins, can be deduced from the well-known equation:

$$kr^2\frac{d^2\theta}{dr^2}+2k\frac{d\theta}{dr}=r\frac{d\theta}{dt}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

which expresses the fact that the excess of heat flowing into any elementary concentric spherical shell through the inner surface, over the heat flowing out to regions beyond, is equal to the heat stored during the same time in the element. The coefficient, k, is the thermometric conductivity of the medium—that is to say, its thermal conductivity divided by its thermal capacity, c, per unit volume.

We will consider the supply of a constant quantity of heat, Q, under four different conditions:

(1) Instantaneously at the origin.
(2) At the origin at a uniform rate during the time T.
(3) Instantaneously over a spherical surface of radius a.
(4) Instantaneously throughout a spherical volume of radius a.

The following numerical values, appropriate to air as the medium, will be assumed throughout: $k=0{\cdot}5$, $c=0{\cdot}00014$, both in c.g.s. units. The total heat supplied, Q, will be taken as 0·001 calorie, and the original temperature of the medium will be assumed to be 0° C.

I. *Instantaneous Point Source.*

The solution of equation (1) for this case was given by Fourier * in the form

$$\theta=\frac{Q\epsilon^{-r^2/4kt}}{8c(\pi kt)^{3/2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Values of θ, the temperature in degrees centigrade for various values of r and t, calculated from equation (2), are given in Table I.

TABLE I.

t sec.	Temperature at					
	0	·05	·075	·1	·15	·2 cm.
0	∞	0	0	0	0	0
·001	14350	4111	862	97	·2	0
·002	5074	2716	1244	416	20	·2
·003	2762	1820	1081	521	65	3·5
·004	1794	1313	888	514	108	12
·005	1283	999	731	472	135	23
·006	976	793	611	424	150	35

At any distance, r, from the origin the temperature of the air reaches the highest value it can attain there after an interval of time, $t=r^2/6k$.

Thus, at a distance of 0·05 cm. the maximum temperature is reached after 0·00083 sec., and at a distance of 0·1 cm. it is reached after 0·00333 sec.; at this latter distance the temperature of the air never rises higher than about 526°.

If an inflammable mixture of the same thermal properties is assumed to be substituted for the air, and the ignition temperature of this mixture is assumed to be 700°, then the greatest volume of the mixture that can be simultaneously raised (by conduction of heat only) to a temperature not less than this ignition temperature, is approximately that of a

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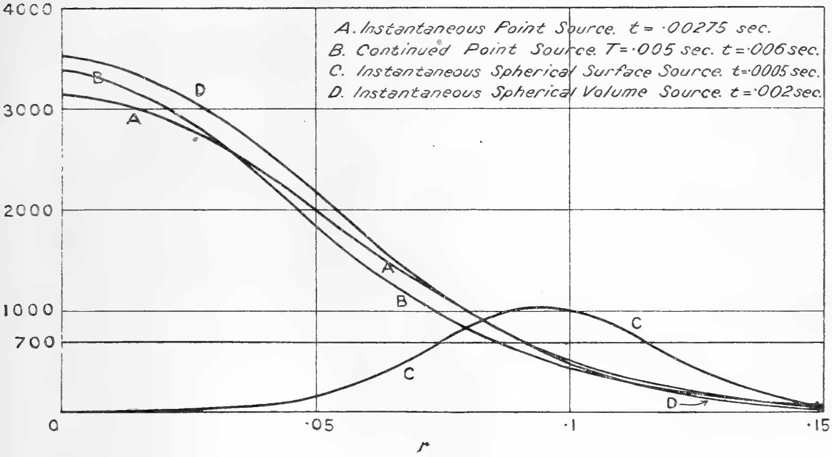
* M. Fourier, *Théorie de la Chaleur*, § 385.

sphere 0·091 cm. in radius, or about 3·16 mm.[3] This volume may be regarded as a measure of the "incendivity" of the instantaneous point source of heat (with respect only to its ability to disseminate heat by conduction), for comparison with the other hypothetical sources shortly to be discussed.

The time at which the temperature of the gas at a distance 0·091 cm. from the origin reaches its maximum (namely, 700°) is about 0·00275 sec. The form of the temperature wave at this time is shown in fig. 1, curve A, in which the abscissæ are values of r, and the ordinates temperatures.

Fig. 1.



The distribution of temperature due to different quantities of heat supplied instantaneously at the origin is easily calculated from Table I., the temperature at any place and time being proportional to Q.

II. *Continued Point Source.*

The solution of equation (1) for the case in which heat is supplied at the origin at a uniform rate q per second for a time interval T is obtained by integration from equation (2). When the time t, for which the temperature is calculated, is less than T, the solution is

$$\theta = q \int_0^t \frac{\epsilon^{-r^2/4kt}}{8c(\pi kt)^{3/2}} dt,$$

which with the substitution $z=r/2\sqrt{kt}$ becomes

$$\theta=\frac{q}{2kc\pi^{3/2}r}\int_{\frac{r}{2\sqrt{kt}}}^{\infty}\epsilon^{-z^2}dz. \quad . \quad . \quad . \quad . \quad (3)$$

When t is greater than T, the solution takes the form :

$$\theta=\frac{q}{8c\pi^{3/2}}\int_{0}^{\mathrm{T}}\frac{\epsilon^{-\frac{r^2}{4k(t-\mathrm{T})}}}{[k(t-\mathrm{T})]^{3/2}}d\mathrm{T}$$

$$=\frac{q}{2kc\pi^{3/2}r}\int_{\frac{r}{2\sqrt{kt}}}^{\frac{r}{2\sqrt{k(t-\mathrm{T})}}}\epsilon^{-z^2}dz. \quad . \quad . \quad . \quad . \quad (4)$$

In Table II. are given numerical values of θ calculated from equations (3) and (4) for a total quantity of heat of 0·001 calorie supplied uniformly during 0·005 sec.—that is to say,

$$q=\frac{\mathrm{Q}}{\mathrm{T}}=\frac{1}{5}\ \text{cal./sec.}$$

TABLE II.

t sec.	Temperature at				
	0	·05	·075	·1	·15 cm.
·001	∞	518	54	3	0
·002	∞	1197	283	58	1
·003	∞	1641	517	154	9
·004	∞	1952	714	258	26
·005	∞	2181	876	358	51
·006	3391	1841	956	444	80
·007	1890	1303	838	470	109

It will be seen from Table II. that after the heat supply ceases, the temperature at points near the origin (for example, at a distance $r=0·075$ cm.) rises a little before falling in consequence of the diffusion of the heat throughout the medium. Again, assuming an inflammable mixture with an ignition temperature of 700° to be substituted for the air, this temperature is approximately the maximum temperature attained at a distance $r = 0{\cdot}0855$ cm., and it is reached after an interval of time $t = 0{\cdot}006$ sec. The temperature wave at this time is shown in fig. 1, curve B. Thus the greatest volume which is raised to at least 700° (by conduction alone) is that of a sphere of radius 0·0855 cm., or 2·62 mm.^3 This volume accordingly represents the incendivity of the continued point source of heat. The incendivity of a point source of total heat 0·001 calorie, uniformly in action over 0·005 sec., is thus about 17 per cent. less than that of an instantaneous point source of the same total heat.

Similar calculations for other values of the time of heat supply T showed that as T is increased, the surface representing the 700° limit continues to shrink, and that as T is diminished, the temperature distribution continually approaches that given by an instantaneous point source (T=0) of the same total heat. The incendivity of a source of small rate of heat supply may therefore be very much less than that of an instantaneous source of the same total heat.

The general conclusions to be drawn from a comparison of Tables I. and II. are: (1) if an inflammable mixture is to be ignited by a given quantity of heat supplied at a point, the more quickly it is supplied the better; and (2) the total quantity of heat supplied by a given source is no criterion as to its incendivity unless the rate of supply also is specified.

III. *Instantaneous Spherical Surface Source.*

The distribution of temperature when the heat is supplied instantaneously and uniformly over a spherical surface has been stated by Lord Kelvin *. In this instance, if a is the radius of the spherical surface source, the temperature at any point distance r from the centre is given by

$$\theta = \mathrm{Q}\frac{\epsilon^{\frac{-(r-a)^2}{4kt}} - \epsilon^{\frac{-(r+a)^2}{4kt}}}{8car\pi^{3/2}(kt)^{1/2}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Some values of θ calculated from equation (5) with a taken as 0·1 cm. and q as 0·001 calorie, are given in Table III.

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* Enc. Brit. 9th ed. Art. "Heat," Appendix. The expression given by Kelvin should, however, be divided by π.

Table III.

t sec.	r cm.				
	0	·05	·1	·125	·15
0	0	0	∞	0	0
·0005	1·8	166	1015	435	55
·001	97	411	718	420	137
·002	416	540	507	347	181
·003	522	527	414	299	182
·004	514	482	356	265	175

As might be expected, the temperature in the neighbourhood of the source falls to small values much more rapidly with the spherical surface source of heat than with the instantaneous point source (Table I.). Thus with the spherical source the temperature, after an interval of time $t=0·002$ sec., is at no point in the medium as high as 700° C. It can be shown that at a time $t=0·0005$ sec., the volume of the spherical shell bounded by the surfaces $r=0·075$ cm. and $r=0·115$ cm. is at or above 700° C. (see fig. 1, curve C). This volume is 4·605 mm.^{3}, which is considerably greater than the greatest volume raised simultaneously to or above 700° by the instantaneous point source, and is 1·76 times as great as the maximum obtained with the continued point source (Table II.). Arguing solely on the distribution of heat by conduction, it is therefore to be expected that the effectiveness of a source of ignition will be improved by spreading it over a surface rather than by concentrating it into a small space. It is also a fair conclusion that a number of simultaneous sparks arranged close together in parallel would be more effective than a single spark of the same length and the same total heat content.

IV. *Instantaneous Spherical Volume Source.*

We arrive at the solution for this case by integration from equation (5). Thus, if q is the heat generated instantaneously per unit volume of a spherical source of radius a, so that $Q=\frac{4}{3}\pi a^3 q$,

$$\theta=\frac{q}{2cr(\pi kt)^{1/2}}\int_0^a x\,dx\left\{\epsilon^{\frac{-(r-x)^2}{4kt}}-\epsilon^{\frac{-(r+x)^2}{4kt}}\right\}$$

$$=\frac{3Q}{4ca^3\pi^{3/2}}\left\{\int_0^{\frac{r+a}{2\sqrt{kt}}}\epsilon^{-y^2}dy-\int_0^{\frac{r-a}{2\sqrt{kt}}}\epsilon^{-y^2}dy\right\}$$

$$-\frac{3Q}{4ca^3\pi^{3/2}}\cdot\frac{(kt)^{1/2}}{r}\left\{\epsilon^{\frac{-(r-a)^2}{4kt}}-\epsilon^{\frac{-(r+a)^2}{4kt}}\right\}\quad . \quad . \quad . \qquad (6)$$

The temperatures given in Table IV. are calculated from equation (6) with $a=0{\cdot}05$ cm. and $Q=0{\cdot}001$ calorie. The initial temperature of the source is 13640° C.

TABLE IV.

t sec.	*r* cm.				
	0	·05	·1	·125	·15
0	13640	13640	0	0	0
·001	7207	3388	284	38	2·5
·002	3530	2174	498	160	40
·003	2162	1518	526	236	88
·004	1493	1130	494	264	124
·005	1105	879	447	268	143

Comparison of this table with Table I. shows that, at the times given in the tables, the temperature at short distances from the centre, due to the spherical volume source, is lower, and at great distances is higher, than that due to the instantaneous point source. The greatest volume raised to or above 700° by the spherical volume source is nearly the same as that raised by the instantaneous point source—namely, the volume of a sphere 0·091 cm. in radius. With the spherical volume source this is effected after a time $t=0{\cdot}002$ sec. The form of the temperature wave at this time is shown in fig. 1, curve D.

It appears, therefore, for the particular values assumed in the above calculation that there is no advantage to be gained, from the point of view of the distribution of heat by conduction, in enlarging the source of heat from a point to a uniformly supplied spherical volume 1 mm. in diameter; and that both are inferior to a spherical surface source of 2 mm. diameter. It is clear, however, that much more effective distributions of temperature can be obtained by further increasing the size of the source of heat. The best possible source of ignition is obviously such a volume of the inflammable mixture as can be raised instantaneously by the given quantity of heat Q to its ignition temperature; any further spreading out of the source, either in space or in time, can only result in a diminution of the volume that is simultaneously raised to the ignition temperature, and no improvement can be attained by altering the shape of the volume initially heated. With $Q=0\cdot001$ calorie, and an assumed ignition temperature of 700°, the volume of the most effective source for ignition is 10·2 mm.^3 (that is to say, the volume of a sphere of radius 0·1345 cm.), a figure which represents the maximum incendivity according to the scale of measurement defined.

The results of the above calculation show that, if a source of ignition be regarded solely as a source of heat, the effectiveness of a given quantity of heat in raising a sufficient volume of an inflammable mixture to a given temperature (by conduction alone) depends essentially upon the manner in which that heat is communicated to the mixture.

Differences in the heat contents of the least sparks of different types capable of igniting a given gas mixture are therefore to be anticipated. To quote a single example, it has been found that the energy necessary to ignite a certain coal-gas mixture by a capacity spark was ·00025 joule, and by an inductance spark ·0006 joule. The ratio of these figures is of the order of magnitude which would be anticipated from a purely thermal theory of ignition (*cf.* discussion of Tables I. and II.). It will be apparent from the foregoing that the observed differences in spark energy required for ignition of a given gas are not in themselves sufficient to warrant the assumption that ignition is due to ionization, as such differences are consistent with a purely thermal theory.

XXXVIII. *The Specific Heats of Ammonia, Sulphur dioxide, and Carbon dioxide.* *By* Prof. J. R. Partington *and* Mr. H. J. Cant *.

IN recent years the theory of specific heats has been prominent, but the subject is still very incomplete. In the case of solids, the work of Planck, Einstein, Nernst, Lindemann, and Debye, based on the Quantum Theory, has resulted in notable advances. In the case of gases, however, the treatment has principally been based on the theory of Equipartition of Energy, which is now known to be of very restricted validity, and fails altogether in the case of solid bodies at low temperatures. The application of the Quantum Theory to gases has been most incomplete, and the results are far from satisfactory.

The determinations described in the present communication were carried out with the object of obtaining reasonably accurate data which might be used in theoretical discussion; the paper deals only with the experimental results, and does not enter into questions of theory, which are deferred until more data are available.

The method employed was that of Kundt, as modified by U. Behn and H. Geiger, the method of filling the gas-tubes being that described by Partington (*Phys. Zeit.* xv. p. 601, 1914). A tube of suitable dimensions is filled with the gas under investigation, and contains also a small amount of some light powder unaffected by the gas. The tube is sealed at both ends, which are as far as possible symmetrical, and is clamped in the middle. When the tube is set in vibration by stroking, it is usually found that the dust figures are very irregular, if any appear at all. Such a tube is chosen that its mass is a little too small to vibrate in resonance with the contained gas. To produce resonance, circular rings cut from thin sheet-lead are cemented on the two ends of the tube symmetrically. The hole in the middle of each ring is to admit the projection at each end, or at one end, of the tube where it was sealed off.

One end of this tube is then brought inside another, slightly wider, tube, open at both ends. This tube is fitted with a cork piston and contains a small quantity of the same powder as the sealed tube. By varying the position of the piston the position for resonance in the air inside the open tube is found, and when the gas tube is set in vibration sharp dust figures are formed in both tubes. The wave-lengths of

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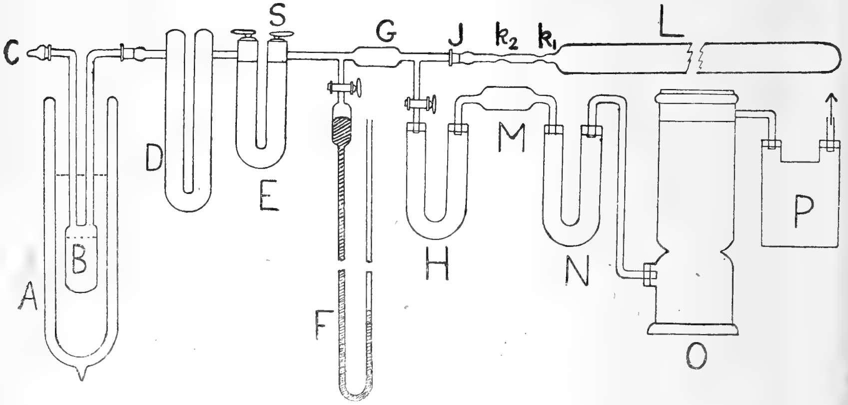
* Communicated by the Authors.

sound of the same frequency can then be determined in the gas and in air.

In the experiments described below a gas tube was used which was about 125 cm. long and with an internal diameter of 4 cm. There was, therefore, no necessity to apply the correction for diameter which is required for narrower tubes (Kundt, *Pogg. Ann.* cxxvii. p. 497, 1866; cxxxv. p. 347, 1868; Kirchhoff, *ibid.* cxxxiv. p. 177, 1867; Thiesen, *Ann. Phys.* xxiv. p. 401, 1907). The tube had practically the same internal diameter throughout, was free from irregularities in the walls, and was straight. It was cleaned with nitric acid, washed and dried. One end was sealed off and blown as nearly hemispherical as possible. To the other end a short tube with a ground connexion, J (fig. 1), was sealed, and the remaining part blown hemispherical as before. The tube was then washed out with a mixture of concentrated sulphuric acid and sodium dichromate, then with dilute nitric acid, and finally several times with hot distilled water quite free from grease. The water was then allowed to drain out by inverting the tube. Complete cleaning is most essential.

Fig. 1.



The powder used was silica. This was prepared by pouring water-glass diluted with its own volume of water into concentrated hydrochloric acid with constant stirring. The jelly formed was then heated on a water-bath for some time, and the acid decanted off. The residue was extracted and washed several times with concentrated, then with dilute hydrochloric acid, and finally with hot distilled water until the liquid was free from iron and chlorides. The silica was dried on the water-bath and afterwards strongly heated in a silica crucible. The perfectly white mass was finely ground in an agate mortar, and the finest powder obtained by shaking through satin. A little of this powder was heated strongly in the silica crucible, and introduced while very hot into the gas tube, which had previously been dried out as described below.

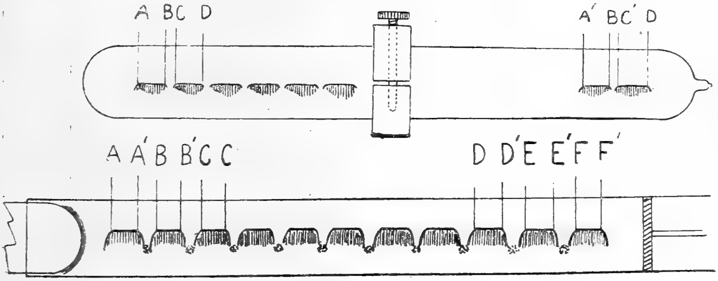
In order to obtain satisfactory dust figures, it is absolutely essential that the moisture adhering to the surface of the glass tube should be removed. Warming with a flame is useless. The tube was packed with asbestos into an iron tube which covered it completely, the part J alone projecting. The iron tube was strongly heated by a combustion furnace, whilst the air in the gas tube was pumped out through drying tubes containing calcium chloride and phosphorus pentoxide. The temperature should be as high as it is safe to go without softening the tube, say 350°–400° C. Dry air was then allowed to pass slowly into the tube through the drying apparatus, and the process of exhaustion and filling with dry air repeated several times. The tube was allowed to cool still connected with the drying tubes, and when cool a small quantity of the silica powder introduced as rapidly as possible. The exact amount required can be ascertained by trial ; a very small quantity is sufficient. The operation of drying out was then repeated. The first drying cannot be carried out with the silica in the tube, as this leads to adherence of the powder to the glass. The tube was then connected with the apparatus for filling with gas, shown in fig. 1.

This apparatus was entirely of glass, no rubber or cork joints coming in contact with the gas passing into the tube. All taps and connexions were lubricated with vaseline in the case of ammonia and carbon dioxide, and with syrupy phosphorus pentoxide in the case of sulphur dioxide. The ammonia gas was obtained from a cylinder of anhydrous liquid ammonia of 99·8 per cent. purity, and was re-liquefied in a 50 c.c. condensing vessel B, of thin glass, contained in a Dewar vessel A filled with solid carbon dioxide and ether. The vessel B was then disconnected from the supply cylinder and the ground cap C attached. The whole apparatus was then brought into connexion with a Geryk pump through P. Tube D contained broken sticks of caustic soda and E quicklime, in the case of ammonia; in the case of sulphur dioxide both tubes contained phosphorus pentoxide. Tube G contained dry glass wool. The pump was protected by the second set of drying tubes. H contained quicklime and N sticks of caustic soda, in the case of ammonia; in the case of sulphur dioxide and carbon dioxide both contained phosphorus pentoxide. There was dry glass wool at M, and O contained pumice soaked in sulphuric acid in the case of ammonia, otherwise soda-lime. P was intended to collect any liquid passing over from O.

The liquid in B was kept in the freezing mixture, and most of the air in the apparatus removed by the pump. At the temperature used, the liquid ammonia or sulphur dioxide had no appreciable vapour-pressure. The tap connecting H and G was turned off and the vessel A removed. Ammonia or sulphur-dioxide gas from B gradually filled the whole apparatus to atmospheric pressure, as indicated by the mercury manometer F. The vessel A was then restored to the freezing mixture, and the process of exhaustion and filling repeated four times. In this all the air in the apparatus above the tap on H was removed. The tap S was then turned off, B immersed in the freezing mixture, and the apparatus exhausted to the highest degree possible. The tap above H was turned off and, by removing the freezing mixture and turning on tap S, the tube L was allowed to fill with gas to atmospheric pressure. This process was repeated six times, and by this time the tube contained very pure gas obtained by the fractionation of the liquid in B. The pressure was then adjusted to 76 cm. and the gas tube sealed off at K_2, about 4 in. from the end of the wider tube. The portion K_1K_2 was then sealed off, leaving only a very short length on the tube L. The parts K_1 and K_2 had previously been thickened and drawn out for convenience in sealing off. The portion of tubing K_1K_2 was then carefully opened under water, in the case of ammonia and sulphur dioxide, or potash in the case of carbon dioxide. In all cases the liquid filled the tube completely without leaving the slightest bubble of air.

The gas tube was then held in a horizontal position by gripping it in the middle with a clamp (fig. 2). This clamp consisted of two rectangular blocks of wood, each having a semicircular recess cut in it and lined with felt. The two blocks were hinged, and at the opposite side fitted with a large screw passing freely through the upper block and engaging in a thread in the lower block. This clamp was fixed firmly to a long plank screwed to the bench. The gas tube, gripped by the clamp, was supported in a horizontal position by two prisms of cork placed between the tube and the board. These prisms were placed at the nodes near the ends, when the latter had been found by trial, and did not interfere with the vibration of the tube. The tube was caused to vibrate, emitting a strong shrill note, by stroking it at one end with a rag moistened with water at the temperature of the air in the room. The weight of the tube was adjusted to resonance by attaching with marine glue circular rings of sheet lead, hammered into a hemispherical shape over a hard wood form, so as to fit exactly the ends of the tube. Exact resonance was attained by varying the temperature of the room slightly by opening the window until the dust figures were sharp, the tube being allowed sufficient time to take up the temperature of the surrounding air.

Fig. 2.



The air tube was 150 cm. long and 4·25 cm. internal diameter. It was fitted with a cork piston movable by a glass rod, and was firmly clamped in a horizontal position with its axis along that of the gas tube.

By shaking the gas tube and then tapping, the powder was caused to settle in the form of a thin uniform line extending the whole length of the tube. Even with every precaution to avoid moisture, the silica adheres slightly to the glass, but this does not interfere with the measurements. The gas tube was now clamped with the silica at the bottom, then by loosening the clamp slightly the tube was rotated through about 45°. Silica was introduced into the air tube by spreading the powder on a ruler, which, on tilting, left a line of powder on the glass. The tube was rotated as described. Fresh silica was used in the air tube for each experiment.

The temperature was recorded by a thermometer placed alongside the tubes.

After a few trials, resonance was obtained in both tubes. The position of the nodes was marked by strips of gummed paper, and the distances were then measured by a calibrated meter rule.

The diagram of the dust figures shown in fig. 2 and the Table I. show how the mean wave-lengths were calculated.

TABLE I.

AMMONIA.

No. of nodal distances measured.	Whole distance in cm.	Mean for pairs cm.	λ/2 cm.
9 AC′	92·60	92·63	10·292
9 BD′	92·66		
8 AA′	82·31	82·27	10·284
8 BB′	82·23		
8 CC′	82·51	82·46	10·308
8 DD′	82·41		
4 AE	40·96	41·04	10·260
4 BF	41·12		
3 GC′	30·86	30·86	10·287
3 HD′	30·86		
		Mean	10·286

AIR.

No. of nodal distances measured.	Whole distance in cm.	Mean for pairs cm.	λ/2 cm.
9 AF	74·39	74 39	8·266
9 A′F′	74·39		
8 AE	65·98	66·23	8·279
8 A′E′	66·48		
7 AD	57·68	57·92	8·274
7 A′D′	58·16		
8 BF	65·88	65·98	8·248
8 B′F′	66·08		
7 CF	57·65	57·68	8·240
7 C′F′	57·71		
		Mean	8·261

Keutel (Diss., Berlin, 1910) has shown that no advantage is gained by reducing the results by the method of least squares, and that no correction need be applied for the moisture in the air of the tube, or other impurities in the air.

From the wave-lengths in the gas and in air, the ratio of the specific heats, $\kappa = c_p/c_v$, may be calculated. For an ideal gas:

$$u^2 = \frac{p}{d}\kappa', \quad \ldots \ldots \ldots \quad (1)$$

where u is the velocity of sound in the gas, p the pressure, d the absolute density, and κ' the ratio c_p/c_v for an ideal gas with constant c_v.

By combining (1) with the general gas equation $px = \mathrm{RT}$, we find

$$\kappa' = u^2 \cdot \frac{\mathrm{M}}{\mathrm{RT}}, \quad \ldots \ldots \ldots \quad (2)$$

where M is the molecular weight, R the gas constant, and T the absolute temperature. If u is in cm. per sec.,

$$\mathrm{R} = 8{\cdot}2 \times 10^7 \text{ erg}/1^\circ.$$

If (2) is applied to an actual gas, the value of κ' obtained does not give c_p/c_v, but is a purely arbitrary number. The true ratio c_p/c_v may, however, be calculated from κ' by the equation

$$\kappa = \kappa'\phi, \quad \ldots \ldots \ldots \quad (3)$$

where ϕ is given by Nernst (*Theoretische Chemie*, vii. Aufl.):

$$\phi = 1 - \frac{9}{64}\pi\tau(1 - 6\tau^2). \quad \ldots \ldots \quad (4)$$

This equation is based on the equation of D. Berthelot for the compressibility of gases under pressures not far removed from atmospheric. The values of π and τ are calculated from the critical pressure, p_c, and critical temperature (absolute), T_c, as follows:

$$\pi = p/p_c\,; \quad \tau = \mathrm{T}_c/\mathrm{T}\,^*. \quad \ldots \ldots \quad (5)$$

The difference of the two molecular heats is given by

$$\mathrm{C}_p - \mathrm{C}_v = \mathrm{R}\left(1 + \frac{27}{16}\pi\tau^3\right); \quad \ldots \ldots \quad (6)$$

also based on Berthelot's equation, and given by Nernst (*loc. cit.*).

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* *Mém. du Bureau internat. des Poids et Mesures*, xiii. (1907).

From (1) we obtain, for two ideal gases,

$$\kappa_2' = \kappa_1' \frac{d_2}{d_1} \left(\frac{\lambda_2}{\lambda_1}\right)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where λ is the wave-length of sound in the gas and d the ideal density.

From c_p/c_v and $C_p - C_v$ we can calculate C_p and C_v separately.

Ammonia.—The following table gives the results with ammonia.

TABLE II.

Number of Experiment.	$\frac{\lambda}{2}$ NH$_3$ cm.	$\frac{\lambda}{2}$ air cm.	κ'.
1	10·286	8·261	1·277
2	10·340	8·281	1·284
3	10·334	8·277	1·284
4	10·316	8·254	1·287
5	10·326	8·295	1·276

Mean $\kappa' = 1·285$. Mean temperature 14°·5 C.

p for $NH_3 = 115$ atm. ; $T_c = 403°$ abs. (Kaye and Laby's Tables.) Thus, from (4) ϕ for NH_3 under the conditions of experiment is 1·0185. From (6) we find $C_p - C_v = 2·065$ g. cal. The values of κ_2' given in all the tables in this paper are calculated by (7) with κ_1' for air taken as 1·403 (Partington, *Phys. Zeit.* xiv. p. 969, 1913), and d_2/d_1 is the ratio of the molecular weights (air=28·98). Thus, for ammonia ($d_2/d_1 = 17·03/28·98$),

$$\kappa = c_p/c_v = 1·308 \; ; \; C_v = 6·70 \text{ g. cal.} \; ;$$
$$C_p = 8·77 \text{ g. cal. (all at } 14°·5 \text{ at 1 atm.).}$$

Keutel (*loc. cit.*) carried out a series of experiments similar to those described above, but he filled his tubes directly from the supply cylinder and corrected his results by Van der Waals's equation. He gives 1·302 and 1·304 as the uncorrected and corrected results, respectively, for c_p/c_v at 20° at 1 atm. Schöler (*Ann. Phys.* [iv.] xlv. p. 913, 1914), also using Behn and Geiger's modification of Kundt's method, obtained the values 1·287 (uncorrected) and 1·305 (corrected) at 20° and 1 atm. The "corrected" value was obtained merely by using the experimental ratio d_2/d_1 in (7) instead of the ratio of the molecular weights. Schweikert (*Ann. Phys.* [iv.] xlviii. p. 593, 1915) reverted to the original method of Kundt. At 19°·0 and 1 atm. he gives 1·3006 as the value of c_p/c_v.

These results are not comparable, since they have been calculated by different methods. In the following table, and in the corresponding ones for the other two gases, the results have therefore been re-calculated, using the value $\kappa = 1·403$ for air and applying the corrections by Berthelot's equation. Although the latter probably does not apply with extreme exactness in the case of easily liquefiable gases (it is known to apply exactly to carbon dioxide under the given conditions), yet the deviations are so small as to be quite inappreciable in the present case. The corrections are believed to be of a much higher order of accuracy than those applied by the previous experimenters themselves, who used methods open to objection. It may be mentioned that much accurate experimental work on the subject of the present communication has been completely vitiated, either by the assumption of the laws of ideal gases or by improper methods of correction. Many of the values quoted in books of tables are in error from this cause.

Table III.

Ammonia. 1 atm. pressure.

Author.	t° C.	$\lambda/2$ NH_3 cm.	$\lambda/2$ air cm.	κ'.	ϕ.	$\kappa = c_p/c_v$.	$(C_p - C_v)$ g. cal.	C_p g. cal.	C_v g. cal.
Keutel ...	20	11·370	9·075	1·294	1·0174	1·317	2·061	8·56	6·50
Schöler ...	20	11·837	9·496	1·281	1·0174	1·303	2·061	8·86	6·80
Schweikert.	0	u NH_3= 413·5 m. per sec.	u air= 331·9 m. per sec.	1·279	1·0218	1·307	2·079	8·85	6·77
Cant and Partington.	14·5	10·320	8·274	1·285	1·0185	1·308	2·065	8·77	6·70

Keutel's result for c_p/c_v appears to be a little too high; the rest are in satisfactory agreement.

Sulphur dioxide.—The gas was taken from a siphon of liquid, re-liquefied and fractionated as described. The measurements were carried out at 1 atm. and 13°·2 C. The following table gives the mean values for three experiments.

TABLE IV.

Number of Experiment.	$\lambda/2$ SO_2 cm.	$\lambda/2$ air cm.	κ'.
1	5·152	8·117	1·249
2	5·142	8·099	1·250
3	5·156	8·125	1·248
		Mean.........	1·249

$$p_c \text{ for } SO_2=78\cdot9 \text{ atm.} ; \quad T_c=428^\circ\cdot4 \text{ abs.} ;$$

$$d_2/d_1=64\cdot06/28\cdot98 \;.\; (C_p-C_v)=2\cdot128 ; \quad \phi=1\cdot0332.$$

Therefore

$$\kappa=c_p/c_v=1\cdot290 ; \quad C_p=9\cdot47 \text{ g. cal.} ;$$

$$C_v=7\cdot34 \text{ g. cal.: all at } 13^\circ\cdot2 \text{ C. at 1 atm.}$$

Thibaut (*Ann. Phys.* xxxv. p. 347, 1911), using Behn and Geiger's method, found at 20° and 1 atm. $c_p/c_v=1\cdot258$. He used the experimental values for the densities of air and sulphur dioxide in (7) without further correction.

Schöler (*loc. cit.*) gives under the same conditions 1·237 uncorrected and 1·265 corrected, calculated in the way described.

Schweikert at 0° and 1 atm. gives 1·2664 corrected.

The values have been re-calculated as described above, and are given in the following table.

TABLE V.

Sulphur dioxide. 1 atm.

Author.	t° C.	$\lambda/2$ SO_2 in cm.	$\lambda/2$ air in cm.	κ'.	ϕ.	$\kappa=c_p/c_v$ corr.	C_p-C_v g. cal.	C_p g. cal.	C_v g. cal.
Thibaut ...	20	5·190	8·250	1·228	1·0308	1·266	2·118	10·08	7·96
Schöler ...	20	5·999	9·511	1·233	1·0308	1·271	2·118	9·93	7·82
Schweikert.	0	u SO_2= 209·4 m. per sec.	u air= 331·9 m. per sec.	1·234	1·0385	1·282	2·149	9·77	7·62
Cant and Partington.	13·2	5·150	8·114	1·249	1·0332	1·290	2·128	9·47	7·34

Carbon dioxide.—The parts A, B, C of the filling apparatus were removed and replaced by a strong bolt-head flask fitted with a rubber stopper and glass tube. The tube had a T-shaped piece, connected with the drying tube D and with a screw-clip and short piece of pressure tubing on the other arm of the T. Solid carbon dioxide, obtained from a cylinder of liquid in the usual way, was filled into the flask, which was wrapped with thick flannel to hinder transmission of heat. The tube D contained phosphorus pentoxide. The filling of the gas tube was carried out as described previously, except that, each time the tap S was closed, the screw-clip was adjusted to allow the gaseous carbon dioxide forming in the flask to escape through a piece of capillary tubing attached to the pressure tubing. The clip was tightly screwed up before S was opened. The experiments with this gas were carried out at 20° C. and 1 atm., and the results were as follows:—

TABLE VI.

Number of Experiment.	$\lambda/2$ CO_2 cm.	$\lambda/2$ air cm.	κ'.
1	6·39	8·21	1·290
2	6·39	8·20	1·293
3	6·37	8·19	1·288
4	6·36	8·18	1·287
		Mean	1·290

$$p_c \text{ for } CO_2 = 72{\cdot}9 \text{ atm.}; \quad T_c = 304^\circ{\cdot}4 \text{ abs.};$$

$$d_2/d_1 = 44{\cdot}00/28{\cdot}98.$$

Thus

$$\phi = 1{\cdot}0110; \ \kappa = c_p/c_v = 1{\cdot}303; \ C_p - C_v = 2{\cdot}037;$$

$$C_p = 8{\cdot}76 \text{ g. cal.}; \quad C_v = 6{\cdot}72 \text{ g. cal.}$$

This result is in good agreement with the value found by Partington (*loc. cit.*) by the method of adibatic expansion: viz., 1·302 at 17°. The values found by other experimenters are shown in the following table.

TABLE VII.

Carbon dioxide. 1 atm.

Author.	t° C.	$\lambda/2$ CO_2 in cm.	$\lambda/2$ air in cm.	κ'.	ϕ.	$\kappa = c_p/c_v$ corr.	$C_p - C_v$ g. cal.	C_p g. cal.	C_v g. cal.
Thibaut ...	15	7·404	9·518	1·288	1·0116	1·303	2·039	8·77	6·73
Schöler ...	20	7·397	9·505	1·290	1·0110	1·303	2·037	8·76	6·72
Schweikert.	0	u CO_2= 257·6 m. per sec.	u air= 331·9 m. per sec.	1·283	1·0139	1·301	2·048	8·85	6·80
Cant and Partington.	20	6·378	8·195	1·290	1·0110	1·303	2·037	8·76	6·72

Summary of Results.—The ratio of the specific heats $\kappa = c_p/c_v$ ammonia, sulphur dioxide, and carbon dioxide have been determined by a method depending on the relative velocities of sound in the gases and in air. The specific heats were calculated. Berthelot's equation of state was used in all calculations. The following results were obtained at 1 atm. pressure.

TABLE VIII.

	Ammonia at 14°·5 C.	Sulphur dioxide at 13°·2 C.	Carbon dioxide at 20° C.
c_p/c_v	1·308	1·290	1·303
C_p	8·77 g. cal.	9·47 g. cal.	8·76 g. cal.
C_v	6·70 g. cal.	7·34 g. cal.	6·72 g. cal.

The authors wish to express their thanks to the Department of Scientific and Industrial Research for a maintenance grant to one of them (H. J. C.), and to the authorities of East London College for a grant which contributed to defraying the expense of the work. The experiments described were submitted as part of a Thesis for the degree of M.Sc. of London University by H. J. Cant.

East London College,
University of London.

XXXIX. *The Absorption of the K X-rays of Silver in Gases and Gaseous Mixtures. By* P. W. Burbidge, *M.Sc.* (*N.Z.*), *B.A.* (*Cantab.*), 1851 *Exhibition Scholar, Trinity College, Cambridge* *.

THE published results of experiments on the ionization of mixtures of gases † show discrepancies from the results expected on the accepted theory that the ionization is due to corpuscles ejected by the Röntgen rays from the atoms of the mixture. It seemed worth while, in view of the failure of other explanations, to test directly the assumption that the absorption of the energy necessary to eject these corpuscles was independent of the association of the gases in the mixture—*i. e.*, that this "ionization absorption" is an atomic phenomenon and therefore in a gaseous mixture strictly additive. From the well-known results of the direct test with solids and liquids, this assumption for gases seemed quite probable and received support from the work of H. Moore ‡, who has calculated absorption coefficients on this basis, but, since the accuracy of Moore's comparison was necessarily very limited, it was judged advisable to make a few direct experiments. During the course of these, some measurements of absorption coefficients were also obtained.

Experimental Methods.

(1) *X-Rays.*

As a source of strong homogeneous radiation an attempt was made to utilize the direct rays from a palladium anticathode, but the nature of the radiation was too dependent on the hardness of the bulb, and the method was therefore abandoned and secondary silver characteristic rays (K type) used instead. These were excited in the usual manner, and the best arrangement for the greatest homogeneity was determined by obtaining a series of absorption curves in aluminium. Using a bulb with a platinum anticathode, it was found best to have an alternative spark-gap of 2·7 cm. (between points), a thin plate of silver (99·9 per cent., ·075 mm.), and a filtering screen of silver foil (·026 mm.). The bulb was placed in a large lead-lined box directly above the radiator, which was again in a small lead box from which

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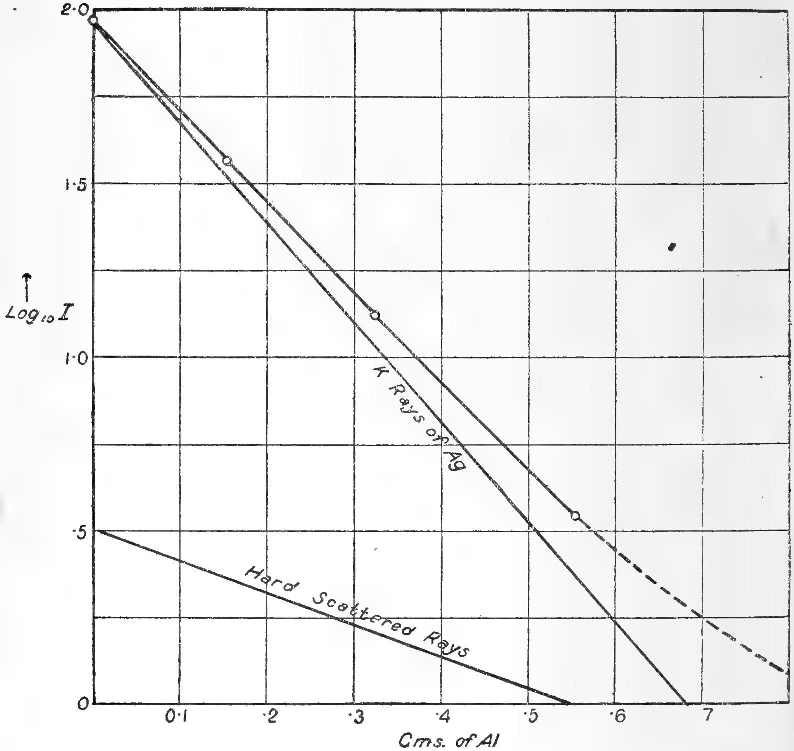
* Communicated by Prof. Sir J. J. Thomson, O.M., F.R.S.

† Barkla and Simons, Phil. Mag. Feb. 1912; Barkla and Philpot, Phil. Mag. June 1913.

‡ H. Moore, Proc. Phys. Soc. June 1915; also E. A. Owen, Proc. Roy. Soc., xciv. A, 1918.

a lead tube allowed the silver rays to pass out to the absorption chamber (fig. 2). Direct radiation from the bulb fell on the silver plate only, and scattered radiation from surrounding walls was reduced to a minimum.

Fig. 1.—Absorption-Curve of X-Rays.



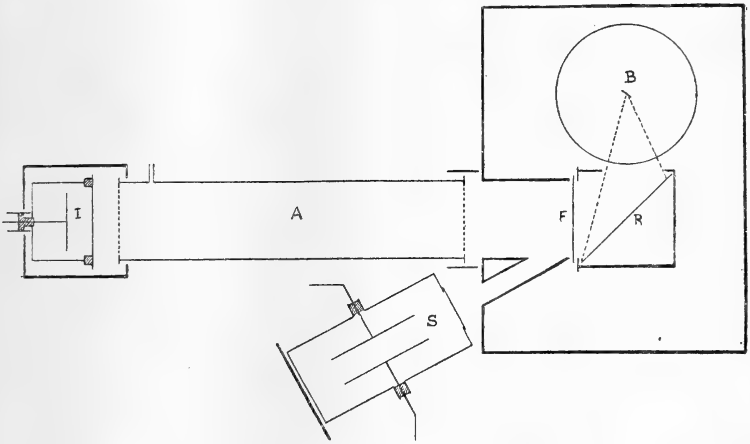
Absorption curves of the rays were determined by placing sheets of aluminium betweem the absorption chamber and the large lead box. The curve for the rays used (fig. 1) showed considerable homogeneity to exist. The radiation appeared homogeneous till 95 per cent. was absorbed, the effective coefficient of absorption in aluminium, μ_{Al}, being 6·01. Assuming the mean for silver K rays in aluminium to be 6·6 (corresponding to Barkla's figure 2·5 for μ/ρ, the mass absorption coefficient), the curve can be analysed into two straight lines corresponding to radiations with $\mu=6·6$

and initial intensity 96 per cent., and $\mu = 2{\cdot}34$ and initial intensity 4 per cent.*

(2) *Measuring Apparatus* (see fig. 2).

To determine the absorption produced by various gases in the absorption chamber, a ratio method was used in which the intensity of the main beam after passing through the chamber was compared with the intensity of a beam of similar rays passing always unaltered into a standard ionization vessel.

Fig. 2 (to scale).



I—main Ionization chamber; S—standard; A—Absorption chamber; F—silver filter; R—silver radiator; B—X-ray bulb.

The absorption chamber was a stout aluminium cylinder, 50·8 cm. long, 12 cm. in diam., with each end closed with two circular aluminium plates, 4 mm. thick, holding between them a thin aluminium sheet † (·1 mm.). These two plates for each end were drilled with the maximum number of holes (8 mm. diam.) so that the X-rays could pass through the thin sheet in the "windows" thus formed. Three long rods ran the length of the cylinder and bolted the ends against the cylinder, and all the joins were cemented with a plastic wax made with resin, beeswax, and a little turpentine.

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* The analysis was made from the absorption curve (log I/thickness of Al), generally graphically, but also by the analytical method given by Sir J. J. Thomson, Phil. Mag. Dec. 1915.

† Celluloid and vaselined parchment were both attacked by SO_2.

Thus arranged the vessel withstood the strains due either to evacuation or to an internal pressure of 2 atmospheres, without developing leaks.

The main ionization vessel was a short brass cylinder placed so that the rays entered through the aluminium potential plate and fell on the brass electrode connected to the measuring electroscope. The front aluminium plate was ·4 mm. thick, to absorb any soft L radiation from the lead used in screening.

The standard ionization vessel was a long brass cylinder with parallel aluminium plates (14 × 4 cm.) between which the beam of rays passed. Both ionization vessels were sealed with air inside. The difference in structure between the two vessels resulted in surprisingly good detection of changes in the homogeneity of the X-rays, this being shown by the variation in the ratio of the ionizations in the two vessels.

The electroscopes used were of the Wilson tilted type, and for greater constancy of readings were enclosed in wooden boxes to minimize convection currents in the leaf-chamber, and had earthing keys consisting of weighted sharp knitting-needles pressing into brass or copper. These keys were both connected to a potentiometer, the middle of which was earthed, and were arranged to lift simultaneously, so as to isolate both measuring systems at once. Corrections were made for natural leak and for insulation leaks.

(3) *Gases.*

The gases used were air, sulphur dioxide, hydrogen, carbon dioxide, sulphuretted hydrogen, oxygen, and methyl iodide. In all cases but the last they were passed slowly through two calcium-chloride tubes (15 × 1·5 cm.). The absorption chamber was evacuated with a water-pump, filled with dried gas, and the operation repeated once at least, generally twice. The pressure of gas in a U-tube mercury manometer gave the proportion present. No rubber connexions were used in standing contact with the gases.

The sulphur dioxide was obtained from the commercial liquid; the carbon dioxide from marble and pure hydrochloric acid solution, acid spray being absorbed in a tube of glass wool moistened with sodium-carbonate solution; the methyl iodide was evaporated into the evacuated chamber from liquid in an attached air-free bulb, the liquid boiled at 41°·9 and the pressure of vapour in the chamber kept constant after the tube connecting with the liquid was closed.

The absorption chamber in this experiment was evacuated with an oil-pump to < 1 mm. Hg; the stopcocks were lubricated with a brominated grease from paraffin wax and vaseline, to avoid leaks from action of the iodide vapour.

II. Results.

(1) *Absorption Coefficients.*

If I_1 is the measure of the intensity of the rays entering the ionization vessel (as recorded by the observed potential on the electroscope) for a pressure of gas p_1 mm. of mercury in the absorption chamber, I_2 is the corresponding measure for p_2 mm. pressure, μ is the linear absorption coefficient of the gas at atmospheric pressure P, d the length in cm. of the absorbing path,

then $$I_2 = I_1 \cdot e^{-\mu d \left(\frac{p_2-p_1}{P}\right)}$$

i. e., $$\mu = \frac{2\cdot3\times760}{d}\times\frac{\log_{10} I_1/I_2}{(p_2-p_1)}.$$

The quantity d is the measure of the average length traversed in the chamber—in this experiment the difference between this and the axial length (50·8 cm.) was negligible. Inserting the value for d, we have

$$\mu = 34\cdot4\frac{\log_{10} I_1 - \log_{10} I_2}{(p_2-p_1)}.$$

This coefficient represents the total loss suffered in the particular apparatus. Some of the radiation scattered in a forward direction is collected by the ionization chamber, and thus reduces the absorption as measured. In the lack of definite data for scattering by various elements at different wave-lengths, a rough estimate of the amount so collected was made, assuming the mass scattering coefficient to be ·2, using Crowther's* distribution figure and taking a mean value for the solid angle of rays collected. Adding this correction, a value for the total absorption is obtained.

A further correction is necessary for the lack of homogeneity of the rays used. As will be seen from figure 1, over the range of absorption used, the rays appear homogeneous but with a lower absorption coefficient in aluminium

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* J. A. Crowther, Proc. Roy. Soc. lxxxvi. A, 1912.

than silver rays. From the relation

$$\tau/\rho = \mathrm{A} \,.\, \lambda^x$$

(where τ/ρ is the mass ionization absorption, λ is the wave-length, A is a constant for a particular material, and x is a universal constant, approx. 3), then

$$\tau_1/\rho_1 = \mathrm{A}_1\lambda^3, \quad \tau_1'/\rho_1 = \mathrm{A}_1\lambda'^3$$
$$\tau_2/\rho_2 = \mathrm{A}_2\lambda^3, \quad \tau_2'/\rho_2 = \mathrm{A}_2\lambda'^3$$

whence $$\tau_1/\tau_2 = \tau_1'/\tau_2',$$

as Barkla and Collier * found.

Hence the correction can be made for the different wave-lengths, since τ_1 for the gas is measured with the rays used, τ_2 for aluminium is also measured (6·14), and τ_2' for aluminium for silver K rays (6·62) is known.

The corrected values are tabulated :—

Gas.	Press. Range (mm. Hg).	μ observed.	μ (corr. for scattering).	τ $(\mu - \cdot 2\rho)$.	τ (corr. for Rays).	μ corr. $(\tau + \cdot 2\rho)$.	ρ.	τ/ρ.	μ/ρ.
Air ...	1450	·00059	·00068	·00042	·00045	·00071	·00129	·35	·55
CO_2...	1450	·00091	·00105	·00065	·00076	·00110	·00198	·35	·55
SO_2...	1440	·0069	·0072	·00662	·00715	·00773	·00288	2·50	2·70
CH_3I.	130	·0905	·1060	·1047	·114	·1153	·00638	17·9	18·1

In fig. 3 are shown the present experimental results together with those of Barkla and Collier (*loc. cit.*) and of E. A. Owen †, the graph representing the variation of log τ/ρ with log λ.

The figures given by Owen in his paper are for total absorption, as he used a narrow beam ; those of Barkla and Collier are given as total absorption, but since probably they used a fairly wide beam there would be some correction necessary. However, for this purpose the value of the mass scattering coefficient, ·2, has been subtracted from both sets of values. Siegbahn ‡ has plotted similarly some of Barkla

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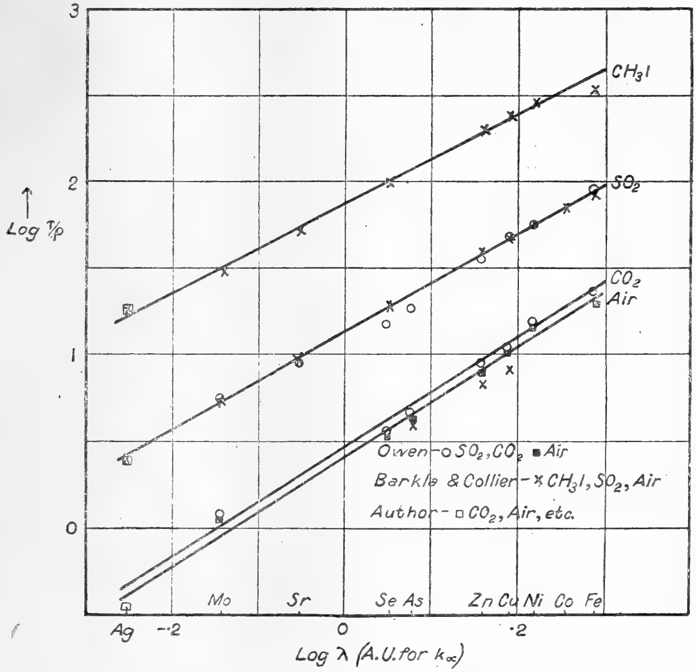
* Barkla and Collier, Phil. Mag. June 1912.

† E. A. Owen, Proc. Roy. Soc. lxxxvi. A, 1912.

‡ Siegbahn. *Phys. Zeitschr.* 1914; Siegbahn gives these values, by mistake, as Owen's.

and Collier's values for the total absorption coefficient. The wave-length chosen is for the K_α doublet.

Fig. 3.



From the slopes of the lines the constant x, of the equation $\tau/\rho = A\lambda^x$, has the values 2·60 for methyl iodide, 2·80 for sulphur dioxide, and 3·13 for air and carbon dioxide.

(2) *Absorption in Mixtures.*

Three mixtures were used—air and sulphur dioxide, carbon dioxide and sulphur dioxide, methyl iodide and air—and, in addition, the absorption in the mixture sulphur dioxide and hydrogen (equal volumes) was compared with that in the mixture, sulphuretted hydrogen and oxygen (equal volumes); each of these latter mixtures has the same number of atoms of each element but the chemical combination is different.

In the case of any mixture the absorption, if additive, will be in accord with the relation

$$I_2 = I_1 \, . \, e^{-(\mu_1 p_1 + \mu_2 p_2)d/P}$$

i.e., $(\mu_1 p_1 + \mu_2 p_2) = 34{\cdot}4 \, (\log_{10} I_1 - \log_{10} I_2)$.

(*a*) For the first two mixtures, μ_1 and μ_2 were measured, p_1 and p_2 observed, and the value of the left-hand side of the equation was compared with that of the right:—

Gases.	Pressures (mm. of Hg).	$\mu_1 p_1 + \mu_2 p_2$	Right side above equation.
SO_2 ...... Air	739 710	5·52	5·64
SO_2 ...... Air	703 729	5·28	5·29
CO_2 ...... Air	741 700	5·50	5·63
CO_2 ...... SO_2	735 705	5·53	5·54

(*b*) In the experiment with methyl iodide and air, the absorption due to the additional air was determined.

Gases.	Pressures.	μ air.	μ air (determined above).
CH_3I ...... Air	111 1384	·00066	·00059
CH_3I ...... Air	94 1421	·00065	·00059

The agreement is not so close as before, possibly because the decrease of ionization due to extra absorption by the air was difficult to measure. Owing to the chemical activity of the iodide, it could not be mixed with denser gases like sulphur dioxide which would give greater change in ionization.

(*c*) For the chemical combination test, the sulphuretted hydrogen (from iron sulphide and hydrochloric acid) was found, on analysis over caustic soda, to contain 7·5 per cent. of hydrogen. This was allowed for in the two mixtures, so that in each case there was a small surplus of hydrogen. The ionizations resulting after absorption in each mixture were determined in quick succession.

Mixture.	*Ionization.*	
700 mm. $SH_2 + 700\ O + 57H$	66·1	Excess of H estimated by analysis.
700 mm. $SO_2 + 700\ H + 57H$	66·5	Excess of H added.

The hydrogen was generated from zinc and sulphuric acid and was passed through moist glass wool to eliminate acid spray. The oxygen was 99 per cent. pure from a commercial cylinder.

Some time after the experiment had been completed, a paper by Simons * was noticed in which he has recorded the same result for this particular comparison.

The results of these four direct tests show that the assumption of additive absorption in gaseous mixtures and compounds is justified.

Summary.

(1) The total absorption coefficient of silver K radiation has been measured in air, carbon dioxide, sulphur dioxide, methyl iodide.

(2) Using this silver K radiation, it has been shown by direct test on four mixtures that the absorption in gases is atomic (as in the case of solids and liquids) and therefore additive in mixtures and compounds.

My thanks are due to Professor Sir J. J. Thomson for suggesting this research and for his interest in the experiments.

XL. *Note on the Absorption of Narrow X-ray Beams.* By P. W. Burbidge, *M.Sc.* (*N.Z.*), *B.A.* (*Cantab.*). 1851 *Exhibition Research Scholar, Trinity College, Cambridge* †.

THE experimental data on the scattering of X-rays at small angles is somewhat meagre and the following rough experiments were done, at the suggestion of Professor Sir Ernest Rutherford, to ascertain whether at very small angles there was any very large scattering effect which may have escaped observation.

The principle of the method is that used by Rutherford and Nuttall ‡ in determining the scattering of α rays—the absorption of the rays in some medium is measured (1) with a wide-angle beam, (2) with a very narrow beam. In the case of X-rays the ideal arrangement for the former case would be to have the radiating point at the centre of a sphere and to measure the absorption in a surrounding spherical shell. If the coefficient so determined were then subtracted

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* Simons, Univ. of Durham Phil. Soc. Proc., 1912–13.

† Communicated by Sir E. Rutherford, F.R.S.

‡ Rutherford & Nuttall, Phil. Mag. vol. xxvi., Oct. 1913.

from the greater value obtained by passing a very thin pencil of the same radiation through the same medium, the difference would approximate to the coefficient of scattering in the medium *. Such an ideal comparison is experimentally difficult, but it is possible to compare the absorption of a wide-angle beam with that of a very narrow one, and so detect any very large small-angle scattering.

Experimental Arrangements.

The source of X-rays was a palladium bulb run under constant conditions (*i. e.*, speed of mercury break, currents in primary and secondary of the coil, alternative spark-gap [1 cm. between 1 cm. spheres, corresponding to 27,000 volts]) to give the maximum of palladium radiation, which was then filtered through silver foil to transmit mainly the palladium K_α line †. This gave a fairly homogeneous primary radiation (see figure) the absorption of which in sulphur dioxide was measured by a ratio method, with reference to an unaltered beam of rays in the manner described in the previous paper ‡.

For the absorption chamber, a wide brass cylinder was used, 29·7 cm. long by 11 cm. in diam., lined with aluminium 1 mm. thick. In experiments with the wide-angle beam the full aperture of this vessel was used, the ends being of perforated aluminium as described in the previous paper. The narrow beams were obtained by using two sets of horizontal slits, in 3 mm. lead, placed one at each end of the absorption chamber and independent of it; one set had 4 mm. slits, the other ·6 mm. The chamber had special ends, each fitted with a continuous narrow aluminium window; these special windows and the independence of the slits from the absorption chamber were necessary to avoid errors from mechanical displacements consequent on pressure changes in the chamber.

Two separate ionization vessels were used corresponding to the sections of the X-ray beams. Any characteristic radiation (Aluminium K or Lead L) excited in the passage of the palladium rays was reduced to a negligible amount by the time the interiors of the ionization vessels were reached. Owing to the small ionization from the narrow beams, sulphur dioxide was used in the ionization vessel with the 4 mm. beam, and methyl iodide vapour mixed with air in the

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* The actual total scattering coefficient would be obtained if a correction could be made in the spherical case for the average increase of path of the scattered rays.

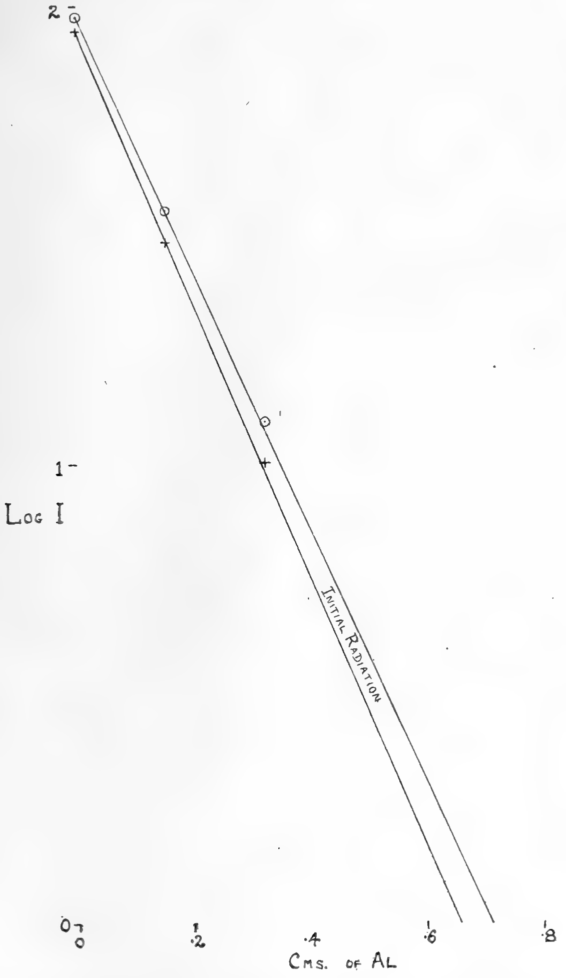
† Hull, Phys. Rev., Series 2, vol. x., 1917.

‡ See p. 383.

case of the ·6 mm. The methyl iodide had always an effect on the insulation even when the gas mixture was well dried*.

The plane angle of rays entering the ionization chamber

Fig. 1.—Log Absorption Curves of X-rays.



in the wide-angle beam was 13°. The rays fell also on the sides of the absorption chamber, but a check experiment, in which the beam was limited by a lead screen so that it just

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* Amber, sealing-wax, and rubber are attacked by the iodide; the insulation of quartz was impaired; quartz coated with sulphur answered fairly well but was affected—it recovered if SO_2 was passed through.

filled the solid angle subtended by the ionization chamber, showed that there was at most a 4 per cent. difference (due probably to the increase in path of rays scattered from the sides). For the 4 mm. slits the vertical plane angle of the beam was ·5°, and for the ·6 mm., ·07°.

Results.

In the table below the results obtained are tabulated, the absorption coefficient being reduced to atmospheric pressure. The comparison between the various beams was made in two stages—the absorption of the wide beam being compared with that of the 4 mm. beam, and this latter then with the ·6 mm. beam. The coefficients for the two narrow beams were almost identical, a small increase of 1 per cent. being shown, on the average, for the finer beam.

Slit.	Plane Angle of Beam of Rays.	Mean μ.	μ/ρ ($\rho=\cdot00288$.)
Wide	13°	·0072	2·50
4 mm.	·5°	·0077	2·69
·6 mm.	·07°	·0078	2·71

The use of a gas-filled bulb and the consequent variation of the quality of the X-rays necessarily limited the accuracy of the experiments, and all that can be said is that there does not appear to be any large small-angle scattering of the rays, a result confirming and extending to smaller angles the direct method used by Crowther [*].

My thanks are due to Professor Sir Ernest Rutherford for the suggestion of this research and for the interest he has shown during its prosecution.

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[*] J. A. Crowther, Proc. Camb. Phil. Soc., vol. xvi., 1911.

XLI. *A Note on Beta Rays and Atomic Number.*

By J. L. Glasson, *M.A., D.Sc.*[*]

1. ALL workers on the passage of fast β rays through matter have noted that the uncorrected absorption coefficient appears to be a periodic property of the weight of the atom. A résumé of the present state of our knowledge of this subject is to be found on pages 227 to 234 of Rutherford's 'Radioactive Substances,' where the results of Crowther and of Schmidt are fully stated and discussed. Crowther's curve connecting μ/D with atomic weight seems to show that there are two effects at work, one of which increases steadily throughout the series of the elements while the other is a periodic function of the atomic weight. The investigation of Schmidt (*Ann. d. Phys.* xxiii. p. 671, 1907; *Phys. Zeit.* x. p. 929, 1909; *Phys. Zeit.* xi. p. 262, 1910) has disentangled two effects. An outline of Schmidt's theory is given by Rutherford together with a complete table of his results. Schmidt finds that the passage of β rays through matter can be usefully considered in terms of two coefficients, the absorption coefficient α, and the scattering coefficient β; and he reaches the conclusion that the absorption coefficient α is directly proportional to the density (D), and inversely proportional to the cube root of the atomic weight (A), whereas the scattering coefficient β is directly proportional to the product of A and D. Schmidt finds that $\alpha = \mathrm{C}_1\mathrm{DA}^{-\frac{1}{3}}$ and $\beta = \mathrm{C}_2\mathrm{AD}$, and considers that C_1 and C_2 are universal constants of matter for a given radiation. Professor Rutherford interprets these results to mean that α is proportional to the cross section of the atom and β to the volume of the atom. Schmidt believed that his results proved that there was no periodic effect either in α or in β, and that his results were at variance with those of Crowther.

2. In view of recent tendencies it appears desirable to express Schmidt's results in terms of atomic number, and this is done in the following table. It is found that several obvious discrepancies disappear and the regularities become more obvious. Guided by analogy with the α ray case, it seems likely that the results will be easier to interpret if instead of measuring the coefficients in reciprocal centimetres as Schmidt does, we use the atomic absorption and scattering coefficients defined by the relations

$$a = \frac{\alpha \mathrm{A}}{\mathrm{D}} \quad \text{and} \quad b = \frac{\beta \mathrm{A}}{\mathrm{D}}.$$

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[*] Communicated by Prof. Sir E. Rutherford, F.R.S.

The values of the atomic coefficients are shown in the last two columns of Table I., and their values plotted logarithmically against atomic numbers are shown in fig. 1.

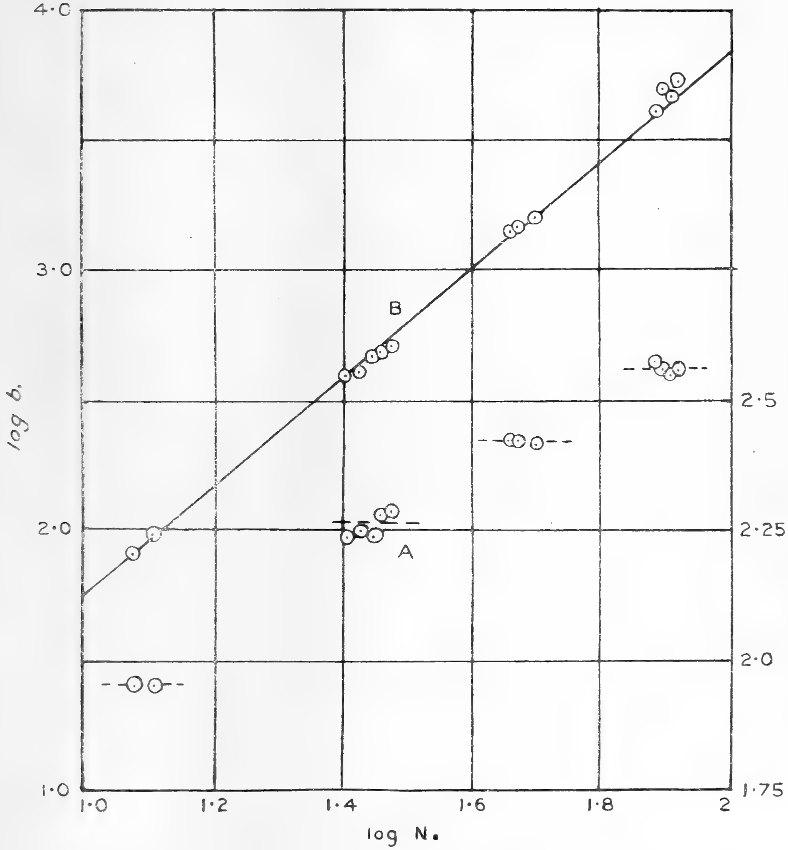
TABLE I.

Symbol.	At. Wt. A.	Density D.	At. No. N.	Schmidt's values.		Atomic coefficients.	
				α	β	a	b
Mg ...	24·4	1·74	12	6·30	5·76	89	81
Al ...	27·1	2·65	13	8·65	9·63	89	99
Fe ...	55·9	7·8	26	24·0	55·9	172	400
Co ...	59·0	8·5	27	25·7	60·0	178	417
Ni ...	58·7	8·9	28	26·1	70·5	172	465
Cu ...	63·6	8·93	29	27·0	70·0	192	496
Zn ...	65·4	7·19	30	21·6	56·9	196	518
Pd ...	107	11·9	46	30·0	160	268	1432
Ag ...	108	10·5	47	26·0	144	268	1480
Sn ...	119	7·3	50	15·6	100	260	1630
Pt ...	195	21·5	78	41·0	468	372	4240
Au ...	197	19·3	79	36·2	480	368	4910
Pb ...	207	11·4	82	19·3	266	350	4820
Bi......	208	9·8	83	16·3	254	348	5400

3. THE ATOMIC ABSORPTION COEFFICIENT.—The figures in the penultimate column of the table do not increase regularly as one proceeds to elements of higher atomic number, but tend to group themselves about four different values, being approximately constant for elements in the same period of the periodic table. This is shown graphically in fig. 1, curve A. Unfortunately the elements used by Schmidt are not well enough distributed to give a complete idea of the shape of the curve ; by analogy with other periodic curves we may expect the missing elements to show intermediate maxima. But it is a remarkable fact that the values for these four groups are almost exactly in the ratio 1 : 2 : 3 : 4. This may be merely coincidence, but in any case it seems to be a consequence of Schmidt's work, that the atomic absorption coefficient is dependent chiefly on the arrangement of the electrons in the atom and not so much on their total number. In view of the importance this result would possess if it could be definitely established, it is highly desirable that Schmidt's results should be confirmed and extended, if possible by an experimental method which does not involve so many theoretical assumptions.

It is obviously possible to draw a straight line through the points of curve A which fits fairly well, and this is in effect what Schmidt did. He was thus led to deny the existence of any periodicity in the absorption coefficient. But when exhibited as they are here it seems most likely that the curve is really periodic, and that Schmidt's conclusions were only rendered possible by the fact that he accidentally confined his work to elements which were all grouped very closely about the centres of the periods. I think the work of Schmidt therefore does not establish the conclusions which he drew from it, and that his results really confirm the existence of the periodicity which Crowther had earlier detected.

Fig. 1.



4. The atomic scattering coefficient.—The figures in the last column of the table increase regularly as one

proceeds to elements of higher atomic number. The relationship is exhibited graphically in curve B of fig. 1, in which the values of log b are plotted against log N. The points fall accurately on a straight line, whose equation is $\log b = 2{\cdot}09 \log \mathrm{N} - {\cdot}44$ and therefore $b = {\cdot}36\,\mathrm{N}^{2{\cdot}09}$. The constant of proportionality is of no significance, being merely determined by our arbitrary choice of the centimetre as the unit of length. Provided one does not extrapolate over too great a range of atomic numbers, Schmidt's results agree with the idea that the atomic scattering coefficient is proportional to the square of the atomic number.

This result is predicted by Sir Ernest Rutherford's theory of nuclear scattering, and has been verified for β rays by observations made in a very direct manner by Dr. Crowther. The agreement of Schmidt's results with these direct observations seems to be *prima facie* evidence of the substantial accuracy of his theory and experiments.

Cavendish Laboratory,
Cambridge.
Nov. 3rd, 1921.

XLII. *Reply to* Sir Oliver Lodge's *paper on the Einstein Spectral Shift.*

[Phil. Mag. June 1921.]

SIR OLIVER LODGE'S criticism of my paper on the Einstein Spectral Line effect appears to be sound in so far as my argument is stated more briefly and more roughly than would be justifiable if the work were given as a theorem in Pure Mathematics. Strictly speaking, if $ds = 0$, the limit of $\frac{\delta t}{\delta s}$ does not exist, and there is no differential coefficient $\frac{dt}{ds}$.

In the problem under consideration, however, there is the underlying physical assumption that the path corresponding to an initial velocity c is the limit, as v tends to c, of the path corresponding to an initial velocity v. This assumption appears to be supported by the transformations of the Special Theory of Relativity and it is difficult to imagine any alternative.

Equations (5) and (6) of my paper lead to

$$\left(\frac{du}{d\phi}\right)^2 + \gamma u^2 = \frac{k^2}{h^2}\left[1 - k^{-2}\gamma^{-1}\right]$$

where k and h depend on the initial velocity v but not on the coordinates.

As v tends to c, k tends to infinity. γu^2 is finite, and, except in the case of a beam passing through the centre of the sun, $\frac{du}{d\phi}$ is finite. It follows that the ratio (k/h) must remain finite, and the above equation reduces to

$$\left(\frac{du}{d\phi}\right)^2+\gamma u^2=a^{-2}.$$

University of Queensland,
Brisbane,
August 5th, 1921.

H. J. PRIESTLEY.

XLIII. *The Fundamental Principles of Scientific Inquiry.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

ON p. 373 of the September number of the 'Philosophical Magazine' Drs. Wrinch and Jeffreys accuse me of having stated in my 'Physics' that "only those processes, logical and experimental, are admissible in physics, which are universally agreed to be valid." On pp. 21–22 of that book I intended expressly to disclaim that interpretation of my views, and used against it much the same arguments that Drs. Wrinch and Jeffreys have used. The passage concludes thus:—"The view that I wish to assert is .... that science starts by selecting for its consideration those judgements alone concerning which absolutely universal agreement can be obtained, rejecting unhesitatingly any concerning which there can be any doubt or personal opinion; that at every stage of the reasoning to which it submits these judgements a personal element is introduced, and with it the possibility of error and of difference of opinion; and that its final results, those that represent its greatest achievements and possess the greatest intellectual value, are almost as individual and as personal as the greatest achievements of art."

Drs. Wrinch and Jeffreys probably think that nonsense; but it is not the nonsense that they have imputed to me.

Yours faithfully,
NORMAN R. CAMPBELL.

Nov. 6th, 1921.

GENTLEMEN,—

DR. CAMPBELL mentions on p. 29 of his book three classes of judgments which he believes satisfy his criterion: they include judgments of betweenness in time and in space and judgments of number. We would say that the making of each of these judgments is a logical or an experimental process. We were considering only fundamental judgments, and regret that in criticising the criterion we did not make it clear that he applied it only to those classes of judgments which he treats as fundamental; we apologise if we have misrepresented him on any important matter. We suggest that in our paper the words "as fundamental" should be inserted after "admissible."

We think Dr. Campbell must have misunderstood us, for the only argument we used that has any counterpart on pp. 21–22 of his book was directed against a view that we explicitly stated he did not hold. The argument we directed against the doctrine of universal consent was based on the obvious facts that the fundamental judgments depending on experience are judgments of sensation, each of which is absolutely private to one individual, and that the judgments of others can be utilised only as constituent elements in individual judgments. We did not consider whether judgments about the opinion of others are ever used in science, or even whether they can be correct; we were concerned only to point out that they are not fundamental, and require much further analysis before they can be used in a theory of scientific or other knowledge. This argument stands without alteration.

Yours faithfully,
D. M. WRINCH,
HAROLD JEFFREYS.

1921 December 22.

XLIV. *Notices respecting New Books.*

Meteorology: an Introductory Treatise. By A. E. M. GEDDES, O.B.E., M.A., D.Sc., Lecturer on Philosophy in the University of Aberdeen. [Pp. xx+390, with 20 plates, 103 figures, and 11 charts.] (London, Blackie and Son. 1921. Price 21*s.* net.)

WITHIN recent years the development of meteorology has been so rapid and it has increased in practical importance to such an extent, that this concise and up-to-date introductory treatise is very welcome. In writing a volume of this nature, it is always somewhat difficult to decide what to include and what to omit, and no two authors would adopt exactly the same point of view. Allowing for such personal differences, the author appears to have succeeded in including all that is of importance for the beginner, and in avoiding the development of one part of the subject at the expense of another. The chapters on atmospheric electricity, optics, and acoustics are particularly welcome; much of the matter contained in them is usually omitted from textbooks. The author has wisely emphasized the broad principles of the subject and kept them to the forefront; mathematics has been avoided as far as possible, so that the book can be used by students with little mathematical training. After mastering it, the student should have a clear understanding of the basic principles and be well equipped for the study of more advanced treatises.

The volume is well illustrated by plates and line diagrams; the excellent photographs by Mr. G. A. Clarke, of Aberdeen, illustrating the various types of cloud formation may be specially mentioned. It has a very complete index, and is well printed.

Relativity, the Electron Theory, and Gravitation. By E. CUNNINGHAM, M.A. Second Edition. Pp. 148. (Longmans & Co. 1921.)

Leçons Elémentaires sur la Gravitation d'après la Théorie d'Einstein. By E. M. LÉMERAY. Pp. 93. (Paris: Gauthier-Villars et C^ie^. 1921.)

AMONG the books on Relativity which, despite all the difficulties in cost of production of which we hear so much from the publishing trade, are appearing like "leaves in Vallombrosa," these two deserve very special notice.

What distinguishes Mr. Cunningham is his clear straightforward forcible exposition. We feel that not a word is wasted nor a difficulty slurred over. It breaks no new ground and offers no first-hand criticism, but this makes it especially valuable to the student.

M. Lémeray's book is also a manual for the student. It is an account of the equations which Einstein uses set forth in the clearest and most precise form and without any extraneous explanations.

The Mechanism of Life. By JAMES JOHNSTONE, D.Sc. Pp. ix + 247. (Edward Arnold & Co. 1921.)

THE special interest of this book is the author's attempt to bring biology into general line with the recent development of mathematics and physics. It might seem a far cry from the principle of relativity to the theory of the *élan vital,* yet there is nothing extravagant, or in any sense unscientific, in the association which Prof. Johnstone finds between them. The argument is clear and sustained. It begins with an account of the mechanism of the organism and the scheme of its psycho-physical behaviour, drawn largely from Prof. Sherrington's work. It compares the new mechanistic concept with the old Cartesian mechanism, and shows the change which has been brought about by the new physico-chemical concepts and the modern science of energetics. The author then criticises neo-vitalism, particularly the psychoids and entelechies of Driesch, "vestal virgins dedicated to God and barren," and expounds his own "vital" concept that, *in living processes the increase of entropy is retarded.*

The Emission of Electricity from Hot Bodies. By Prof. O. W. Richardson, F.R.S. Second Edition; pp. viii+320. (Monographs on Physics Series. London: Longmans, Green & Co., 1921.) Price 16*s.* net.

The second edition of Prof. Richardson's book has been brought up to date, in the subjects with which it deals, by the extension of certain sections and the rewriting of others. There is now included an account of von Laue's treatment of the problem of the equilibrium of electron atmospheres in cases in which the volume density effects are not negligible; fuller explanation is given of the deviation, at low voltage, from the three-halves power law of thermionic current. Noteworthy also is the description of the author's recent experiments on the emission of electrons under the influence of chemical action.

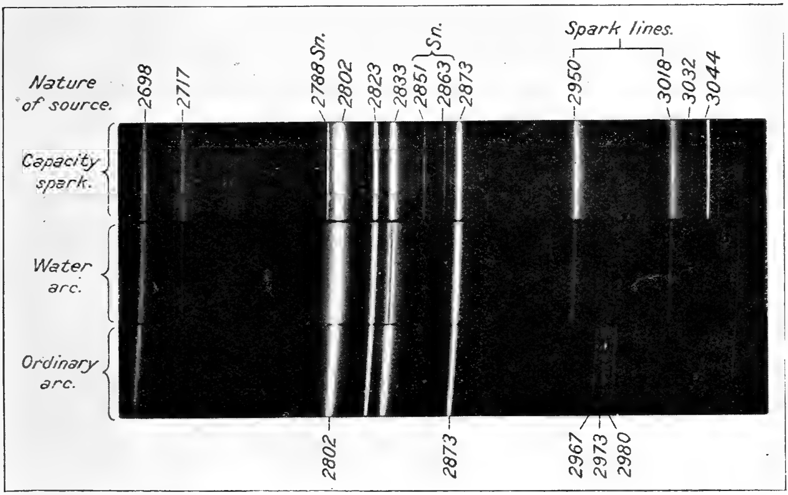
No reference is made to the application of the thermionic current to the rectification and amplification of alternating currents, a short account of which would surely have been of value, if only to help students to realize how purely scientific researches in this subject have made possible the recent strides in the development of radio-telegraphy and radio-telephony; again, many properties of thermionic emission, such as the cooling effect, are now being studied by means of the triodes used in radio telegraphy.

The book remains a store-house of ideas for those who are seeking problems for research, especially in the chapters concerning the emission of positive ions, the emission of ions by heated salts, and ionization and chemical action, subjects which as yet are only in the early stages of development.

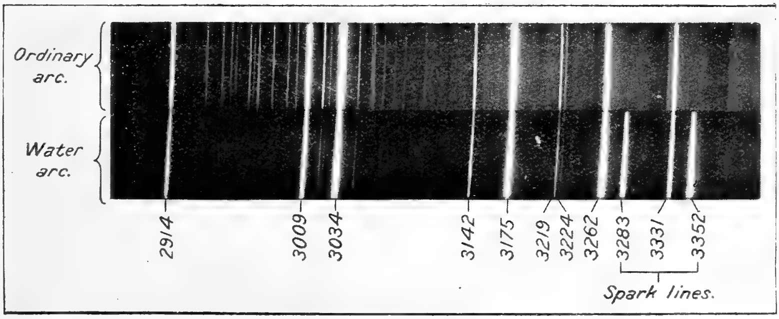
Bibliotheca Chemico-Mathematica: Catalogue of works in many tongues on Exact and Applied Science, compiled and annotated by H. Z. and H. C. S. Two volumes, pp. 964. London: Henry Sotheran & Co. 1921.

This unique work consists primarily of a list of many books on pure and applied science, including mathematics. It was begun in 1906, and was expected to reach about three hundred pages. It developed, however, in the hands of the compilers gradually from a catalogue in the ordinary sense into a storehouse of information about almost all the great works on science. It is indeed a fascinating work, for there are many biographical and historical references both in the descriptions of the various books and in the notes which are appended to many of the entries. The illustrations are exceedingly delightful. They have all been obtained from the actual books by a photographic process, and include, besides facsimiles of illustrations and portraits, textual passages from works of historical importance, many of them produced for the first time. We notice specially an illustration from Boyle's New Experiments Physico-Mechanical (1660), showing his air-pump; and portraits of Torricelli (1715), John Napier (1616), and Thomas Young (1855).

Ultra-violet Spectra of Lead and Tin.

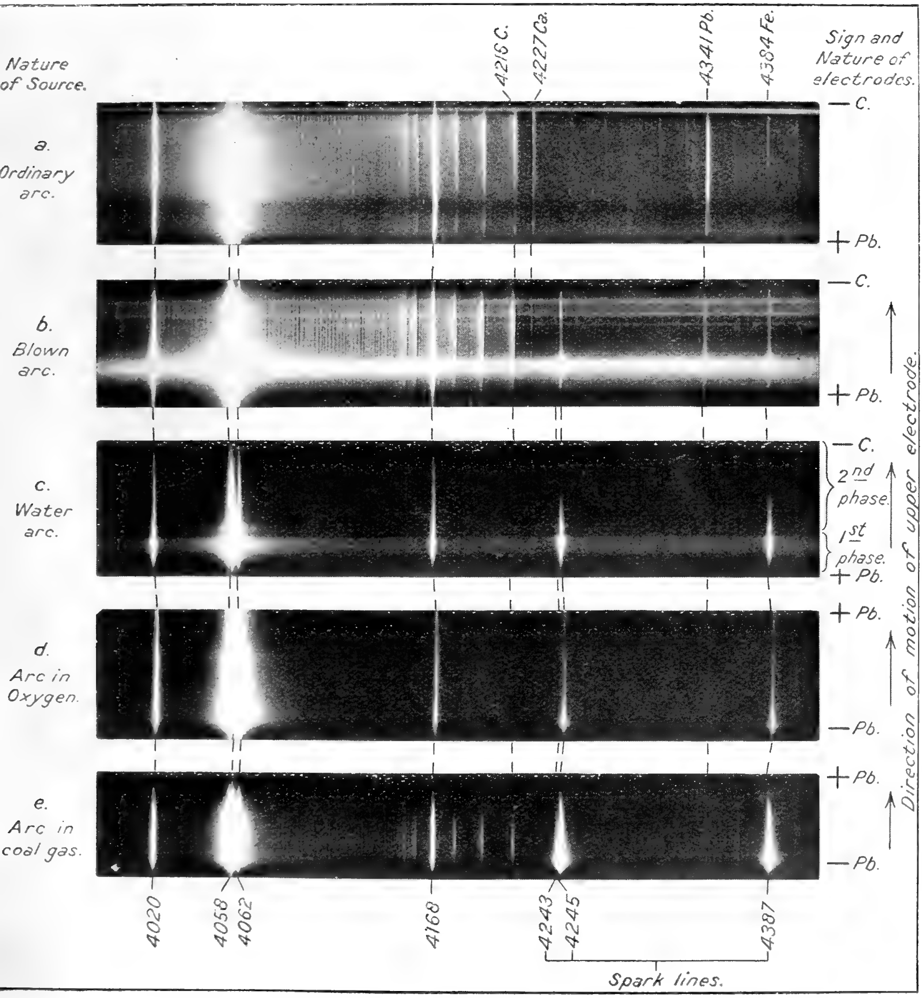


a. Arc and Spark Spectra of Lead.

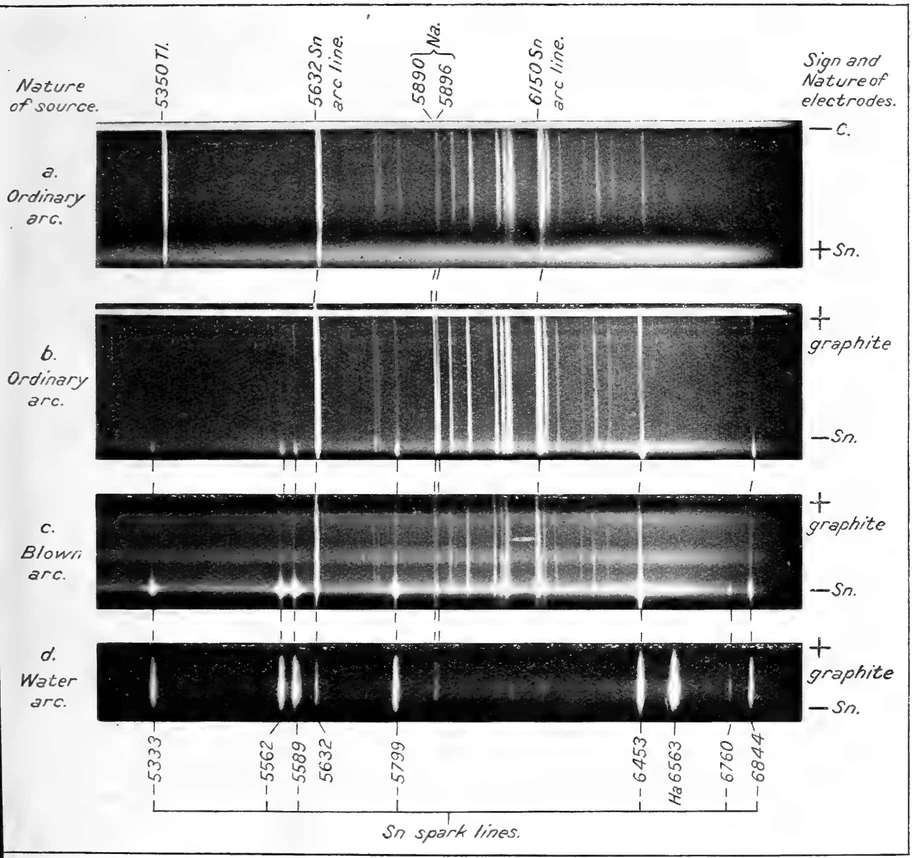


b. Arc Spectra of Tin.

Arc Spectra of Lead.



Arc Spectra of Tin.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

MARCH 1922.

XLV. *The Theory of the Intrinsic Field of a Magnet and the relation of its Magnetic to its characteristic Electric and Thermal Properties.* *By* J. R. Ashworth, *D.Sc.*[*]

Index to Paragraphs.

1. *The Intrinsic Field of a Magnet.*—The theory of the magnetism of a ferro-magnetic material, which regards the intensity of magnetization as analagous to the density of a fluid and treats it as a function of both field strength and temperature, has been developed in some detail in several papers published in this Magazine[†], and an equation has been used for magnetism which is the counterpart of van der Waals's equation of state for a fluid. In this theory it is necessary to introduce an intrinsic field, just as an intrinsic

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[*] Communicated by the Author.

[†] Ashworth, Phil. Mag. vol. xxvii. p. 357; vol. xxx. p. 711; vol. xxxii. p. 334.

pressure has to be introduced in the theory of fluids; and this intrinsic field may be evaluated either from the known facts of intensity of magnetization (I) as a function of the temperature (T) or as a function of the field strength (H), just as the intrinsic pressure in a fluid may be derived from the relation of the density to the temperature or the density to the pressure. In the theory of fluids the constant of the intrinsic pressure (van der Waals's a) has consistent values by whichever method the calculation is carried out, but in the theory of magnetism the constant of the intrinsic field has two values which differ enormously according to the way in which they are derived. For example, if the constant of the intrinsic field is derived from $I = f(T)$ it gives to this field at the highest intensity a value about 10^7 in iron, and similar values in nickel and cobalt, but if it is derived from $I = \phi(H)$ it gives a value of the order of a few units.

We have then to choose between two magnitudes for the intrinsic field of entirely different orders, and the first step will be to find grounds for excluding one or the other.

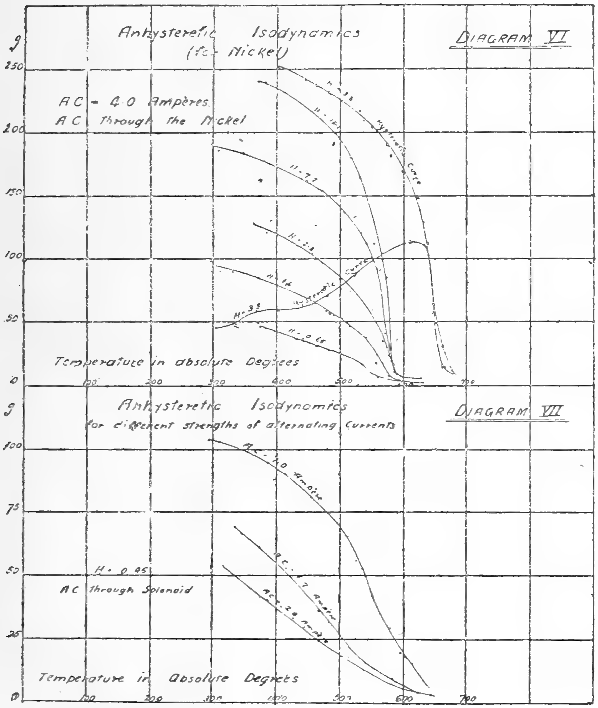
The value of the intrinsic field derived from the equation to the critical temperature in spite of its enormous magnitude has been in general accepted, probably because such a large intrinsic field explains successfully the behaviour of intensity of magnetization under changes of temperature, and also because it may be made to account for the rise in specific heat which the ferro-magnetic metals exhibit when the temperature is raised up to the critical temperature.

But while the effects of temperature on ferro-magnetism are satisfied by the introduction into the equation of an immense intrinsic field, the demonstration that this field is entirely a magnetic field is wanting, and it is allowable to suppose that it is in part, perhaps in greater part, a field of force of some other kind than magnetic.

At the critical temperature the sudden loss of magnetism in ferro-magnetic substances although the most prominent is not the only effect, and the modification which takes place in other properties, such as electrical resistivity, thermo-electric power, and specific heat, is evidence of a change in ferro-magnetic substances which is probably akin to a change of state. If we treat the intrinsic field as the independent variable and the other properties as dependent upon it, then, assuming this field is entirely magnetic and of enormous magnitude, we ought to find some large effects in the dependent properties when this magnetic intrinsic field is varied or suppressed.

There is an interesting change in the magnetic critical temperature, especially prominent in nickel, which can be brought about by the application of an alternating magnetic field, which may be used as a test of the magnitude of the magnetic intrinsic field. If a nickel wire is subjected to an alternating field, then its ferro-magnetism is lost at a temperature 50° to 100° C. lower than its normal critical temperature. Curves illustrating this are shown in the upper diagram of fig. 1, which is taken from a former paper published in this Journal *. Here it is seen that the ferro-magnetic intensity (I), and therefore the intrinsic magnetic field ($a'I^2$), virtually vanish under the action of an alternating field at a temperature of about 560° A. instead of 660° A.; and therefore it is to be expected that the other properties named above, which must be influenced by the withdrawal of such a large large field, will change in some measure at this

Fig. 1.



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* Phil. Mag. vol. xxvii. p. 367.

lower temperature, instead of the normal critical temperature, when an alternating field is applied. The three properties referred to—electrical resistivity, thermo-electric power, and specific heat, which all exhibit abnormal effects up to the magnetic critical temperature,—have been selected for investigation to see if any change occurs under an alternating field at the lowered critical temperature, and in this way to decide if the intrinsic magnetic field has a magnitude large enough to influence these properties.

2. *Electrical Resistivity.*—A length of nickel wire 0·088 cm. in diameter was folded back and forward on itself in six parallel lengths, the ends being joined to stout copper wires which made connexion with the testing apparatus. The nickel wire was placed in a heating tube made of porcelain in which was embedded a spiral of high-resistance wire through which a current of electricity could be passed to generate the requisite temperature. This tube and its contents were put inside a large solenoid of 525 turns of wire, wound in a space of 21·4 cms., through which an alternating current was made to flow, when required, for the purpose of submitting the nickel wire to an alternating field; arrangements were also made so that the alternating field could be applied transversely to the nickel, since the resistivity of nickel is known to change, although to a very small extent, in opposite ways under longitudinal and transverse magnetic fields of great strength. In these experiments the field used was not, however, carried beyond 100 gausses, and the full strength of this field only produced a change of resistance of about one-thousandth of an ohm, a practically negligible quantity. The resistance was measured by a fall of potential method in one set of experiments, and by a Wheatstone bridge method in another set, and the temperature was determined by means of a thermo-junction. Readings of temperature and resistance for very slow heatings and coolings were made with and without an alternating magnetic field in successive experiments, and the field was in one set longitudinal, and in another transverse, to the length of the nickel wire, and in a third set a circular field was applied by running an alternating current through the wire, but in no case was there any perceptible difference in the electrical resistance whether the alternating field was on or off.

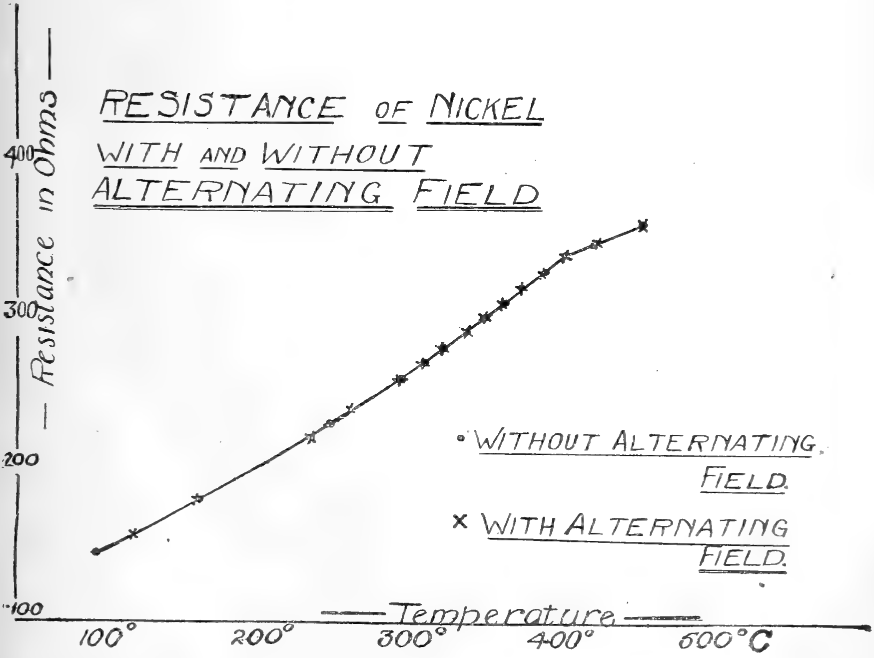
Table I., and the curve in fig. 2 constructed from it, is an example of what takes place in general. The critical temperature for this sample of nickel is a little above 400° C., and

TABLE I.

Variation of Resistance with Temperature in Nickel.

Without alternating Magnetic Field.		With alternating Magnetic Field.	
Temperature C°.	Resistance Ohms.	Temperature C°.	Resistance Ohms.
105	0·145	127	0·157
172	·180	170	·180
244	·220	244	·220
258	·230	271	·240
304	·260	301	·260
318	·270	316	·270
330	·280	330	·280
345	·290	345	·290
359	·300	357	·300
371	·310	569	·310
381	·320	381	·320
396	·330	394	·330
411	·340	411	·340
433	·350	431	·350
461	·360	461	·360

Fig. 2.



under an alternating magnetic field the magnetic critical temperature would be 50° or more lower, but the sharp change of electrical resistance in the neighbourhood of 400° remains the same with or without an alternating field. Now, if under an alternating field an intrinsic field of 10^7 gausses is suppressed at the lower temperature of about 350° C., then the resistivity of the nickel ought to have been altered in two ways: first, from the fact that a field of 10^4 gausses causes a change of about 2 per cent. in the resistivity, a change of field of 10^7 gausses ought to have produced an appreciable effect; and secondly, the sharp bend in the curve, where the temperature coefficient of resistance passes to a normal value, ought to have suffered some displacement towards the new critical temperature. As neither of these anticipated results is realized, these experiments do not support the hypothesis of an intrinsic magnetic field of enormous magnitude.

3. *Thermo-Electric Power.*—The thermo-electric power of both nickel and iron changes as the critical temperature is approached in a very striking way, the straight lines connecting thermo-electric power and temperature curving round through rather more than a right angle, and then, at the critical temperature, bending very sharply back again so as to become roughly parallel to the original direction as seen in fig. 4. If this bending of the thermo-electric lines is due to the gradual diminution and finally sudden loss of an immense intrinsic magnetic field, then a lowering of the critical temperature ought to be in evidence in the curvature of the thermo-electric lines.

A thermo-junction of nickel-platinum was placed side by side with a standard junction of platinum-iridium and platinum in an electric heater inside of which an alternating field of 100 gausses could be maintained. It was then an easy matter to compare accurately the readings of the two junctions with and without an alternating field. A previous experiment showed that the standard junction was uninfluenced by a magnetic field of 100 gausses. The scale readings allowed a potential difference down to 25 micro-volts to be observed, and a temperature of 1° C. to be estimated. Readings taken both up and down the scale were exactly alike whether the thermo-junctions were acted upon or not by an alternating field. A similar experiment carried out with an iron-platinum thermo-junction also showed that there was no difference whether the junction was under the action of an alternating field or not. Thus, again, while the critical temperature for magnetism may be lowered by an alternating field, no corresponding change in the disposition of the sharply curved part of the thermo-electric lines is discernible, and again there is no evidence in support of the hypothesis of an intrinsic magnetic field of enormous magnitude.

4. *Specific Heat.*—The specific heat of the ferro-magnetic metals is not constant, but increases at first slowly and later more rapidly as the critical temperature is approached, and at this temperature falls almost abruptly to a lower value. Weiss [*] considers this change of specific heat to be due to the gradual loss and final destruction of the intrinsic magnetic field of 10^7 gausses, and shows that the thermal energy which has to be supplied, due to such an increase of specific heat, is almost exactly equal to the energy required to destroy a field of this magnitude [†]. If the intrinsic magnetic field is so large as 10^7 gausses, the abrupt drop in the enhanced specific heat ought to take place at a lower temperature when the critical temperature for magnetism is lowered by an alternating field. Experiments on nickel and iron were made with great care to ascertain if this were the fact.

The nickel experiments were made in three ways. First, a nickel wire 0·088 cm. in diameter, wound into a close short spiral, was fixed in a vertical position with a thermo-junction inside it and very nearly in contact with it. This was surrounded with a porcelain tube closed at the top which served as a "jacket" to protect the spiral from draughts of air, and by means of a high resistance wire embedded in the porcelain tube through which a current of electricity could be run, the temperature inside the tube could be suitably regulated. Arrangements were made to heat the nickel by passing a continuous or alternating current through it, and this set up a steady or alternating field as might be required. The change of specific heat was traced by observing the rate of cooling from a temperature a little higher to a temperature a little lower than the critical temperature, and confirmatory experiments were made by observing the rate of heating through a similar interval of temperature. The electrical arrangements for heating the wire and regulating the sur-

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[*] Weiss & Beck, *Journal de Physique*, sér. 4, vol. vii. p. 249.

[†] This result, however, is not a sound argument in favour of a *magnetic* field of 10^7 gausses, inasmuch as the constant of the intrinsic field is derived from considerations of thermal energy.

rounding temperature allowed the rate of cooling or heating to be finely adjusted.

In the second set of experiments a thick nickel wire was folded several times parallel to itself, and the heating was done by passing a current through a spiral of high resistance wire surrounding it, and no current traversed the nickel; the required magnetic field was set up by the heating current, which was either continuous or alternating, and in some experiments by an electromagnet, the field of which, either steady or alternating, was made to act on the nickel longitudinally or transversely. The nickel was, as before, surrounded by the porcelain jacket, and its temperature was determined by a thermo-junction.

In a third group of experiments a block of nickel was used in the form of a short stout cylinder with a small hole drilled half-way through it, into which the thermo-junction fitted nicely, and this was put inside an earthenware pot which could be heated by gas-jets. The magnetizing field was applied by an electromagnet placed on the outside.

The experiments on iron were made on wires only, but in all other respects the apparatus and the conduct of the experiments were the same as with nickel. It will be sufficient to give a brief summary of the results of a large number of observations.

NICKEL.

Method I. (Thin wire traversed by current.)

	Critical Temperature in scale units.
With steady field	19·83
With alternating field	19·72
With no field	19·86

Method II. (Thick wire surrounded with a Solenoid.)

With alternating field	19·26
With no field	19·35

Method III. (Cylindrical Block.)

With alternating field	19·34
With no field	19·50

IRON.

Method II. (Wire surrounded with a Solenoid.)

With alternating field	39·89
With no field	40·06

The temperature of 19·90 scale divisions corresponds to 385° C., one-tenth of a scale division being approximately 2° C. The field, either steady or alternating, was not less than 25 gausses.

The conclusion from these experiments is that the specific heat of neither nickel nor iron shows any change in the critical temperature greater than 2° C. or 3° C., whereas with the alternating fields employed the critical temperature for magnetism must have been lowered very considerably more than this. Hence the loss of the intrinsic magnetic field at this lower magnetic critical temperature is without commensurate effect on the temperature at which the sharp change of the specific heat takes place.

Thus the magnetic properties may be changed in these ferro-magnetic metals without any change of corresponding magnitude taking place in the electrical or thermal properties here considered, and the evidence for an enormous intrinsic magnetic field is not forthcoming.

5. *Corresponding States.*—It has already been remarked that the critical temperature probably signifies a physical change akin to a change of state, and this view suggests that the various properties of the metals which have a critical temperature may behave correspondingly at corresponding temperatures. The observations now obtained on the variation of electrical resistance with temperature together with those of other investigators, and the experiments on the change of thermo-electric power with temperature which have been described above, allow the question to be tested.

(a) *Electrical Resistance.*

Observations of my own on nickel and some on iron by D. K. Morris [*] agree very closely with a set of experiments on nickel and iron carried out carefully by Honda and Ogura [†], and the following table (Table II.) is constructed from their observations on the variation of resistance with temperature.

The absolute temperature of the critical point and the resistance at that point are taken as unity, and other values are treated as fractions of the unit. The graphs in fig. 3 enable the curves of reduced temperature and reduced resistance of nickel and iron to be compared. Up to the critical point (unity on each scale) they follow paths which, although not identical, are similar in form, the maximum difference from exact correspondence being 7 per cent.

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[*] Morris, Phil. Mag. vol. xliv. p. 213 (1897); Phys. Soc. Proc. vol. xv. p. 134.

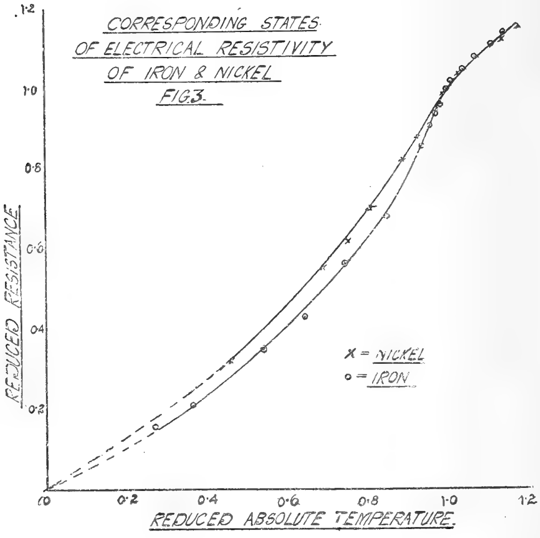
[†] Honda & Ogura, Math. Phys. Soc. Proc. vol. vii. p. 231 (1914).

TABLE II.

Corresponding states for the Resistivity of Nickel and Iron.

NICKEL.				IRON.			
Temp. C°.	$\frac{T}{T_c}$	Resistance Ohms.	Reduced Resistance.	Temp. C°.	$\frac{T}{T_c}$	Resistance Ohms.	Reduced Resistance.
27	·463	·131	·32	18	·275	·503	·16
178	·690	·225	·55	131	·383	·701	·21
216	·749	·254	·62	302	·540	1·113	·35
259	·813	·288	·70	407	·644	1·410	·43
308	·890	·335	·82	514	·739	1·793	·56
330	·924	·359	·88	614	·848	2·203	·68
340	·940	·370	·90	719	·935	2·792	·86
356	·965	·388	·95	740	·955	2·942	·91
369	·990	·405	·99	755	·967	3·052	·94
378	1·00	·412	1·00	762	·976	3·102	·95
381	1·01	·416	1·01	772	·985	3·172	·98
389	1·02	·421	1·02	783	1·00	3·232	1·00
399	1·03	·427	1·04	798	1·01	3·292	1·02
409	1·05	·431	1·05	822	1·04	3·382	1·05
429	1·08	·442	1·08	863	1·07	3·492	1·08
469	1·14	·460	1·12	899	1·11	3·582	1·11
499	1·18	·472	1·15	931	1·14	3·682	1·14

Fig. 3.



Above the critical point the two curves merge into a straight line, which, if equally inclined to both axes, would mean that the resistance at these high temperatures is directly proportional to the absolute temperature.

(b) *Thermo-Electrical Power.*

The thermo-junctions used here were the same as those described in an earlier part of this paper on the effects of alternating fields, and were constructed of nickel-platinum and iron-platinum. The thermo-electromotive force of this particular platinum against lead was separately determined, and the thermo-electric powers, which are set out in Table III., are in micro-volts per degree referred to lead as the standard.

TABLE III.

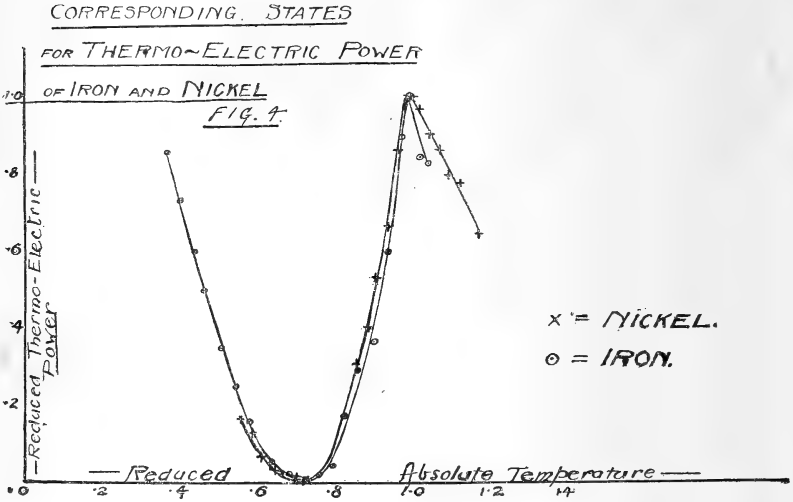
Corresponding states for the Thermo-electric Power of Nickel and Iron.

NICKEL.					IRON.			
Temp. C°.	$\frac{T}{T_c}$.	Micro-volts per degree.	Difference from 23·3.	Reduced $\frac{dE}{dT}$.	Temp. C°.	$\frac{T}{T_c}$.	Micro-volts per degree.	Reduced $\frac{dE}{dT}$.
98	·560	−21·8	+1·5	·158	114	·370	+10·2	·856
119	·591	−22·1	1·2	·126	152	·406	8·7	·731
138	·620	−22·7	0·6	·063	190	·443	7·1	·596
157	·651	−23·0	0·3	·032	228	·467	5·9	·494
176	·677	−23·1	0·2	·021	266	·513	4·1	·345
194	·706	−23·2	0·1	·010	304	·548	2·9	·244
212	·724	−23·3	0·0	·000	342	·584	1·8	·150
266	·813	−21·0	2·3	·242	380	·621	0·6	·050
301	·865	−20·4	2·9	·305	456	·691	0·3	·020
319	·894	−19·5	3·8	·400	494	·727	0·0	0·00
337	·919	−18·2	5·1	·535	532	·763	0·2	·018
354	·945	−17·0	6·3	·662	570	·802	0·5	·043
371	·968	−15·1	8·2	·861	608	·836	2·0	·168
388	1·00	−13·8	9·5	1·00	646	·870	3·4	·285
405	1·03	−14·1	9·2	·967	684	·909	4·3	·361
422	1·05	−14·7	8·6	·903	722	·944	7·1	·596
440	1·08	−15·2	8·1	·861	760	·980	10·6	·889
457	1·10	−15·7	7·6	·798	779	1·00	11·9	1·00
474	1·13	−15·9	7·4	·772	817	1·03	10·0	·840
508	1·18	−17·2	6·1	·641	836	1·05	9·8	·824

The first column for each metal is the temperature in centigrade degrees; the second column is the reduced absolute temperature, the absolute critical temperature of the metal being treated as unity; the third column is the thermo-electric power in micro-volts per degree; and the last column is the reduced micro-volts per degree. The thermo-electric power of nickel is negative to lead, and as it is convenient to have the values positive for comparison with the thermo-electric powers of iron, another, the fourth, column has been inserted in which the numbers in the third column have been converted into positive quantities by subtracting them from 23·3, the maximum thermo-electric power for nickel.

Fig. 4 shows at a glance the results of this table. Up to the reduced critical temperature, unity, the two curves show a general agreement, but above this point there is a considerable divergence which is perhaps due to a change in iron, the molecule of which appears to undergo a subdivision at or near the critical temperature.

Fig. 4.



There is, on the whole, evidence that corresponding states approximately hold for iron and nickel in relation to thermo-electric power.

6. *Theory of an Intrinsic Magnetic and Molecular Field.*—Returning now to the problem of the intrinsic field, the results of the experiments which have just been described lead to the conclusion that the *magnetic* intrinsic field has not the enormous magnitude which has been assigned to it, but on the contrary has probably a very small value. Nevertheless, the effects of temperature on ferro-magnetism demand an

intrinsic field of some kind of very large magnitude; and we are led, therefore, to think of the intrinsic field as the combination of two fields, one a true magnetic field and the other a field of force, not magnetic, arising from molecular forces. These two fields may be distinguished as the magnetic intrinsic field and the molecular intrinsic field.

The extreme ease with which an external magnetic field can turn the magnetic molecules shows that the molecular intrinsic field does not exercise any constraint on the orientations of the molecular magnets, the only rotational constraint to which they are subject being the magnetic intrinsic field *. On the other hand, the molecular intrinsic field controls displacements and translatory movements of the molecules, while the magnetic intrinsic field is not primarily concerned with movements of this kind.

Thermal action produces to and fro displacements which increase as the temperature rises, and at the critical temperature the molecular intrinsic field becomes very small, as witnessed by the fact that elastic forces then very greatly diminish. But, although thermal action does not directly produce rotational vibrations of the molecules, it is a property peculiar to a ferro-magnetic substance that rotational vibrations can be communicated to the molecules from translatory movements *in virtue of the mutual magnetic forces existing between them.* If, for example, we consider a pair of magnetic molecules with their axes in alignment, a to and fro displacement of one, at right angles to this axial line, would produce a forced vibration of the other around its centre, and the magnetic moment of the pair would diminish. Thus it is by the intermediate agency of mutual magnetic forces that thermal action affects the intensity of magnetization. As the to and fro displacements of the molecules become larger and larger with rise of temperature, ultimately losing their oscillatory character at the critical temperature, so the amplitude of the rotational vibrations becomes proportionally wider and wider, and ultimately rotations are developed at or above the critical temperature, and, in consequence, ferro-magnetic properties disappear. Thus, at the critical temperature, both the molecular and the magnetic intrinsic fields become negligible or very small, and the concurrent loss of elastic and magnetic properties at this point finds a ready explanation.

Briefly, the view here taken of the structure and behaviour

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* It is not vital to the view here taken to decide whether the magnetic axis of the molecule is fixed within it, or whether it is free to be orientated within the molecule.

of a ferro-magnetic substance is that it consists of an assemblage of molecules held in definite positions by molecular forces and subject to a molecular intrinsic field; that these molecules are magnets subject to a magnetic intrinsic field; that the molecular field imposes no rotational constraints on the molecular magnets; that a magnetic field does not appreciably affect displacements and translatory movements; that the translatory movements due to thermal action can develop corresponding rotational movements in the molecules *in virtue of the mutual magnetic forces existing between them*, but that rotational movements cannot produce translations; lastly, that the molecular and magnetic intrinsic fields become small and, in effect, vanish at the critical temperature.

7. We now apply these views to the ferro-magnetic equation, which, written in terms of susceptibility, is

$$(\mathrm{H}+a'\mathrm{I}^2)\left(\frac{1}{\mathrm{I}}-\frac{1}{\mathrm{I}_0}\right)=\mathrm{R}'\mathrm{T}, \quad . \quad . \quad . \quad . \quad (1)$$

H being the applied field, I the intensity of magnetization, I_0 its maximum value, T the absolute temperature, and R′ the reciprocal of Curie's constant and such that $\mathrm{I}_0{}^2\mathrm{R}'=\mathrm{R}$ the gas constant.

Instead of the large intrinsic field $a'\mathrm{I}^2$ of the order 10^7 gausses, we substitute for it a small magnetic field $b\mathrm{I}^2$, where b is a small constant, and add a term A′ to the left side which is a function of the molecular field and the temperature, thus

$$\mathrm{A}'+(\mathrm{H}+b\mathrm{I}^2)\left(\frac{1}{\mathrm{I}}-\frac{1}{\mathrm{I}_0}\right)=\mathrm{R}'\mathrm{T}. \quad . \quad . \quad . \quad . \quad (2)$$

Consider first the effect of the temperature varying while the applied field remains constant; then, since thermal agitation induces rotational vibrations, which are a copy of the molecular movements, both may be treated as the *same* function of the temperature, and the equation may be put

$$(\mathrm{H}+b\mathrm{I}^2)\left(\frac{1}{\mathrm{I}}-\frac{1}{\mathrm{I}_0}\right)=\mathrm{R}'\mathrm{T}-\mathrm{A}'=\frac{1}{n}\mathrm{R}'\mathrm{T}, \quad . \quad . \quad (3)$$

where n to a close approximation is equal to a'/b and is numerically of the order 10^7.

From this we get

$$\frac{d\mathrm{I}}{d\mathrm{T}}=\frac{\frac{1}{n}\mathrm{R}'}{-\frac{\mathrm{H}}{\mathrm{I}^2}+b\left(1-2\frac{\mathrm{I}}{\mathrm{I}_0}\right)}=\frac{\mathrm{R}'}{-\frac{n\mathrm{H}}{\mathrm{I}^2}+a'\left(1-2\frac{\mathrm{I}}{\mathrm{I}_0}\right)} \quad . \quad (4)$$

and the first term in the denominator instead of being negligible, as in the former treatment of the ferro-magnetic equation*, is of importance. By thus recognizing the influence of the applied field the correspondence between the curve deduced from the equation and the curve constructed from experimental data is found to be improved.

The equation to the critical temperature (T_c) remains the same as before—namely,

$$T_c = \frac{8}{27} \frac{bI_0}{R'/n} = \frac{8}{27} \frac{a'I_0}{R'} . \quad . \quad . \quad . \quad . \qquad (5)$$

Secondly, let the temperature be constant and the applied field be variable; then, A′ being constant in the absence of external constraints, the right side of equation (3) is constant, and the consequences formerly derived from the ferro-magnetic equation are the same † except that the small factor b replaces the large factor a', with the result that appropriate numerical values of I and H are now obtained.

For example, the relation of I to H is given by the equation

$$\frac{dI}{dH} = \left(\frac{1}{I} - \frac{1}{I_0}\right) \Big/ \left\{\frac{H}{I^2} - b\left(1 - 2\frac{I}{I_0}\right)\right\}, \quad . \quad . \quad . \qquad (6)$$

which shows that hysteresis is in evidence, since the second term in the denominator, involving the small quantity b, is comparable with the first term $\frac{H}{I^2}$. If b were to diminish to a negligible quantity, as it may be made to do under certain conditions, then the equation represents the anhysteretic curve of $I = \phi(H)$.

Again, the equation to the critical field (H_c) is

$$H_c = \frac{1}{27} bI_0^2 ; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

and this correctly gives the critical field as about the order of a tenth of a unit, instead of the order of 10^6 formerly calculated with a' instead of b.

Lastly, when both the molecular and the magnetic intrinsic fields become small enough to be negligible then the ferro-magnetic equation reduces to

$$\frac{H}{I} = R'T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

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* Ashworth, Phil. Mag. vol. xxx. p. 711.

† Ashworth, Phil. Mag. vol. xxxiii. p. 334.

the paramagnetic equation, which applies above the critical temperature.

It remains to show that the abnormal changes of specific heat and of electric resistivity with temperature, which are characteristics of the ferro-magnetic metals, are to be expected if this view of the intrinsic field is adopted.

8. *Specific Heat.*—Since the magnetic molecules are almost entirely free from rotational constraints except for a small magnetic intrinsic field, whilst the constraints under which thermal agitation takes place due to the large molecular field are very great, the energy at ordinary temperatures is almost entirely concentrated in the three degrees of freedom associated with translatory movements; but as the temperature rises, the molecular field becomes weaker, and, when the critical temperature is approached, the energy becomes mainly kinetic, and, *in virtue of the magnetic forces*, it is shared with the additional two degrees of freedom associated with magnetic vibrations and rotations. The specific heat thus increases up to the critical temperature. But just above the critical temperature, experiments show that there is a sudden drop in the specific heat to lower values. This is accounted for by the fact that just at or above the critical temperature, when rotations of the molecules are becoming established, the mutual magnetic forces become very small, and the energy of thermal translatory movements is not as freely communicated to and shared with rotational movements; thermal agitation for higher temperatures will again be mainly confined to translations and the specific heat will fall to a lower value.

The experiments of Pionchon [*] and of Weiss & Beck [†] on the change of specific heat with rise of temperature in ferro-magnetic substances are of great interest in this connexion, and show how far these views are supported by facts.

The following table of specific heats is constructed from their observations:—

	At 17° C.	At Crit. Temp.	Ratio.	Rise.	Fall.	Ratio.
Magnetite	0·165	0·275	3/5	0·110	0·055	2/1
Nickel	0·098	0·153	3/4·7	0·055	0·027	2/1
Iron...............	0·101	0·314	3/9·3	0·213	0·112?	2/1
Cobalt	0·108	0·192?	3/5·4?	0·084?	—	—

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[*] Pionchon, *Ann. Chim. Phys.* 6 sér. xi. p. 23.

[†] Weiss & Beck, *J. de Phys.* sér. 4, vii. p. 249.

The critical temperature of cobalt is about 1100° C., and at this high temperature Pionchon remarks that investigations on specific heats become very difficult and the results must be accepted with some reserve; there are no observations for cobalt in sufficient detail to allow the sudden fall of specific heat above the critical temperature to be traced exactly.

Magnetite gives precisely the required ratio of 3 to 5 for the specific heats at 17° C. and at its critical temperature, but nickel and cobalt have not so exactly this ratio. If, however, the specific heats of nickel and cobalt are compared at corresponding temperatures, the ratios of their specific heats are more nearly alike, and if the chosen corresponding temperature at the lower point is that of iron at 17° C., they are more nearly 3 to 5.

Iron, which has nearly the same specific heat as nickel at 17° C., has an abnormally high specific heat at the critical temperature, which is very nearly the double of that of nickel, and the ratio of the specific heats, namely 3 to 9·3, is thus double the ratio of 3 to 4·7 for nickel. This may be explained by assuming, as before, that the molecule of iron is subdivided at the critical temperature and, if into two parts, the number of degrees of freedom would be doubled and the specific heat would be doubled.

There are two interesting facts which the table brings out, which can be no more than mentioned here: first, the rise or the fall of the specific heat is in each case almost an exact multiple of 0·027, the smallest number; and, secondly, the abrupt fall above the critical temperature is always the half of the rise.

9. *Electrical Resistivity.*—If resistivity is expressed in terms of the heat which is emitted from a conductor, it is evident that a change in the specific heat must produce a change in the resistivity. If s is the specific heat, ρ the resistivity, and t the temperature, then the relation may be put,

$$s=k\frac{d\rho}{dt},$$

where k is a constant.

As long as s is constant, the resistivity will vary linearly with the temperature, but if s increases, the slope of the line, giving the relation of ρ to T, will also increase as the diagram shows (fig. 3). Now, the specific heat of nickel changes, as we have seen, from air temperature to the critical temperature in the approximate ratio of three to five, and we should therefore expect the slope of the line to change in the same ratio. From the reduced curve we get the following results :—

Nickel.—Beginning at air temperature .... $\frac{d\rho}{dt} = 1{\cdot}01$

At the critical temperature .... $\frac{d\rho}{dt} = 1{\cdot}63$

Ratio.............. 3/5

This ratio is approximately the ratio of the specific heats at these temperatures.

Iron.—Beginning at air temperature .... $\frac{d\rho}{dt} = 0{\cdot}72$

At the critical temperature.............. $\frac{d\rho}{dt} = 2{\cdot}15$

Ratio................. 3/9

And, again, this ratio is nearly the ratio of the specific heats.

There seems little doubt that the large and increasing change of resistivity up to the critical temperature is due to the increase of the specific heat; and as this in its turn depends on the mutual magnetic forces between the molecules, we have an explanation of why ferro-magnetic substances exhibit an abnormally large change of resistivity with rise of temperature.

10. Recapitulating, we find from the ferro-magnetic equation, based as it is on a kinetic theory of magnetism, that a magnet possesses an intrinsic field, and that this field must be in magnitude immense if energy effects are taken into account, but only very small if the effects of an external applied field are considered. In short, when the intensity of magnetization is treated as a function of the temperature the intrinsic field must be very large, and when treated as a function of the applied field the intrinsic field must be very small—results which are not consistent with one another.

Further, we find from the effects of an alternating field upon ferro-magnetism—more definitely its ability to lower the critical temperature and at the same time its inability to alter the temperature at which electrical resistivity, thermo-electric power, and specific heat change abruptly—that the intrinsic field cannot be regarded as simply and solely a *magnetic* field of immense magnitude.

This and other difficulties disappear if the intrinsic field is treated as the combination of two fields, one a molecular field, and the other a true magnetic field; the former in magnitude very large and the latter relatively small. It is then assumed that thermal action operates directly on the molecular field by giving rise to translatory movements of the molecules, and that it only indirectly affects the magnetic field by producing rotational vibrations *through the mutual magnetic forces of the molecular magnets*, the rotational movements so developed being a transcription of the translational movements; on the other hand, orientations of the molecular magnets which result from the application of an external magnetic field cannot appreciably influence translations or displacements of the molecules.

This view of a two-fold field explains why the critical temperature is lowered by an alternating magnetic field, while the temperature at which the specific heat changes sharply is but slightly altered; for an alternating field exciting rotational vibrations in the magnetic molecules is highly effective in reducing magnetic intensity by increasing the amplitude of the vibrations, and therefore a lower temperature than the critical temperature is sufficient to bring about the magnetic critical condition; but, on the other hand, an alternating field adds little, or a negligible amount, to the energy of thermal agitation, and so the specific heat is almost unaffected.

This view also gives a reasonable account of the relations of mechanical and magnetic forces, and shows why elastic and magnetic qualities tend to disappear at the same high temperature.

Further, it removes a serious defect in the former statement of the kinetic theory of magnetism and now allows consistent values to be calculated from the ferro-magnetic equation, whether the intensity of magnetization is treated as a function of the temperature or a function of the applied field.

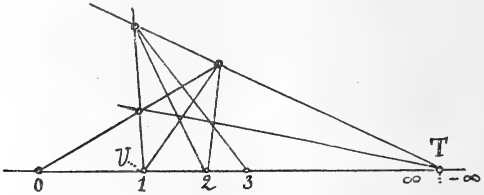
And, lastly, it gives an explanation of the abnormal rise of specific heat, and the abnormally large temperature coefficient of resistivity found in the ferro-magnetic metals.

July 30th, 1921.

XLVI. *The Relation between the Projective and the Metrical Scales, and its bearing on the Theory of Parallels.* By LUDWIK SILBERSTEIN, *Ph.D.*[*]

1. LET us recall briefly the structure of the *projective scale* as given by v. Staudt. OUT being a given segment of a straight line, let us affix to the points O and U of this segment the numbers, labels, or, as we will call them, the Staudtian indices 0 and 1, respectively. The fourth harmonic to 0, 1, T, conjugate to 0, whose construction is shown in fig. 1, will then have the index 2. Continuing this graphical process we shall have the points with indices 3, 4, etc. With equal ease points with any fractional indices can be constructed, and irrational indices are obtained by limit considerations.

Fig. 1.



We need not give here a detailed description of this projective scale construction[†]. Suffice it to say that, the points 0, 1, and T being chosen, the position of a point of the segment OUT having any real positive index n is uniquely determined. The point T itself will have the index $n=\infty$. To points following upon one another from O, via U, to T correspond indices n increasing from 0 to ∞. Beyond O and beyond T we have negative indices, so that the supplement of the segment represents analytically but one domain, $-\infty<n<0$. At T itself, approached from the right, we have $n=-\infty$. (Singular point; discontinuity of n.)

Assuming all these things to be familiar to the reader, let us, however, state explicitly how to any point n of the segment OUT the point with index $-n$ (or the fourth harmonic to O, T, n, conjugate to n) is constructed, since this will be needed in the sequel. Through ∞ and 0 draw any two straight lines crossing in T_y. Take on the segment

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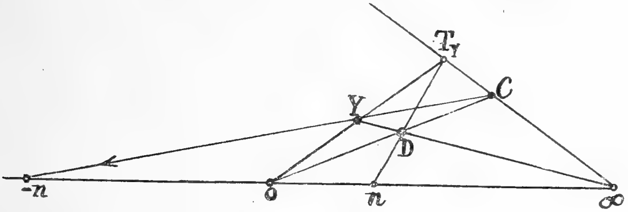
[*] Communicated by the Author.

[†] The reader unacquainted with the subject may consult, for instance, Coolidge's 'Non-Euclidean Geometry,' or the Author's 'Projective Vector Algebra,' London, Bell, 1919.

OT_y any point Y, and join it to ∞. Join n (the given point) with T_y. Let D be the cross of nT_y with $Y\infty$ and let OD cut $T_y\infty$ in C. Then the point whose index is $-n$ will be the cross of CY with the base line (fig. 2), *i. e.* their actual cross if these two lines do intersect, and the ideal point (or pencil centre) determined by these two lines, should they not intersect *.

Fig. 2.



Lastly let us recall that the cross-ratio of any tetrad of collinear points whose Staudtian indices are n_1, n_2, n_3, n_4, is

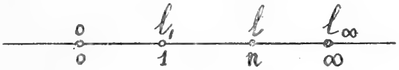
$$(n_1n_2,\ n_2n_4) = \frac{n_1-n_3}{n_1-n_4} : \frac{n_2-n_3}{n_2-n_4}. \quad . \quad . \quad . \quad (1)$$

Thus, for instance, $(02,\ 1\infty) = -1$, this being, from the outset, a harmonic range of points.

2. With this projective or Staudtian scale let us now compare the ordinary *metrical scale*.

Let l_1 be the length $\overline{01}$, *i. e.* the number of metrical units (say, cms.) contained in the segment 01, and l_∞ that contained in the whole segment OUT or in 01∞, as in fig. 3.

Fig. 3.



It is required to find the number l of metrical unit steps leading from 0 to any point of our line whose index is n, the sense from 0 through 1 towards ∞ being taken as that of positive l. In short, it is required to find l as a function of n, such that

$$l(0) = 0, \quad l(1) = l_1, \quad l(\infty) = l_\infty,$$

the latter two being some given finite numbers, such as $l_1 = 3$ and $l_\infty = 100$.

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* *Cf.* 'Projective Vector Algebra.'

The particular form of the function $l(n)$ will depend on the kind of the contemplated straight line, or of the space to which it belongs: Riemannian, Euclidean, or Lobatchevskyan *. In the Euclidean case the question would be answered by simply equating the cross-ratio of the indices [as in (1), with $n_1=0$, $n_2=n$, $n_3=1$, $n_4=\infty$] to the double ratio of the corresponding lengths and by solving for l. But the following way, giving a formula for all three cases, seems preferable.

As is well-known, the Riemannian plane † of curvature $\frac{1}{R^2}$ has all the properties of a Euclidean sphere of radius R, the Riemannian straight lines being replaced by geodesics (great circles); and all Lobatchevskyan formulæ follow from the corresponding Riemannian ones on replacing R by iR.

Consider therefore an ordinary sphere of radius R, and let the previous OUT be a segment of a great circle drawn on it. Since, as can easily be proved, the theorem of Desargues holds for spherical triangles, v. Staudt's construction can be repeated on the sphere, replacing straight lines by great circles, the only caution being that T must not be the antipode of O. Thus we can imagine the scale of Staudtians set up on the geodesic arc OUT. To prevent two points of this segment receiving the same index n, take OUT smaller than a half great-circle. Then giving to U the index 1, the points of this segment will be covered in a one-to-one correspondence by the indices $n=0$ to ∞. (Each of the negative n-values will then belong to two distinct, antipodal points of the supplementary segment, but this will not invalidate our result.)

Now, from the centre of the sphere let four rays be drawn to the points $0, 1, n, \infty$ of the segment. Then, θ being the ordinary geographical longitude reckoned from 0, we shall have $l=R\theta$, $l_1=R\theta_1$, $l_\infty=R\theta_\infty$, and since the cross-ratio of the four rays is equal to that of the four points, we have, by (1),

$$\frac{0-1}{0-\infty}\cdot\frac{n-\infty}{n-1}=\frac{1}{1-n}=\frac{\sin\theta_1}{\sin\theta_\infty}\cdot\frac{\sin(\theta-\theta_\infty)}{\sin(\theta-\theta_1)}.$$

Thus, after easy reductions, and replacing θ by l/R,

$$\cot\frac{l}{R}=\frac{1}{n}\left\{\cot\frac{l_1}{R}+(n-1)\cot\frac{l_\infty}{R}\right\}. \quad . \quad . \quad (2)$$

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* Notice that, according to a famous theorem due to Schur, every projective space is a space of constant curvature, and *vice versa*.

† Or better, a limited portion of it.

This is the required relation between the scale of Staudtians (n) and that of metrical "divisions' (l) set up upon a straight line in any space of constant curvature. For real finite R the formula is ready for the Riemannian straight line; the Euclidean case corresponds to $R=\infty$: and the Lobatchevskyan or hyperbolic one to $R^2<0$.

Leaving out the first case, of no interest for our purpose, let us consider the consequences of (2) for a Euclidean, and then for a hyperbolic segment. The latter will offer some interesting points connected with Lobatchevsky's parallels.

3. *Euclidean segment.*—Putting $R=\infty$, that is, making the ratios of l, l_1, l_∞ to R tend to zero and dividing by R, we have at once

$$l=nl_1 : \left\{1+\frac{l_1}{l_\infty}(n-1)\right\}, \quad . \quad . \quad . \quad . \quad (3)$$

and, conversely,

$$n=\frac{l}{l_1}\cdot\frac{l_\infty-l_1}{l_\infty-l}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

These equations enable us to write down the Staudtian index corresponding to any metrical scale-division, and *vice versa*. If l_1, l_∞ are rational numbers, to every rational l corresponds, by (4), a rational index n, and the corresponding point can therefore be constructed by a finite number of straight-edge operations.

Of particular interest is the value of n corresponding to $l=\infty$ ("point at infinity"). This is by (4)

$$n=1-\frac{l_\infty}{l_1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the same index corresponds to $l=-\infty$. We assume that $l_\infty>l_1$, so that the point corresponding to

$$-n=\frac{l_\infty}{l_1}-1$$

lies *within* the segment OUT. Constructing its negative as shown in fig. 2, we find, through any point Y, *the parallel* to the base line.

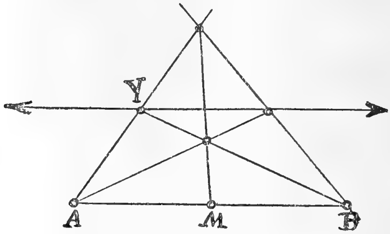
In particular, if $l_\infty=2l_1$, so that $n=1$ is the metrical *mid-point* of OT, we have for the parallel (*i. e.* for $l=\pm\infty$)

$$n=-1,$$

whence the known construction of the Euclidean parallel to a bisected segment, as a sub-case of the construction represented by (5).

It will be well to restate this result:—The knowledge of the mid-point M of a segment AB enables us to draw through any point Y the parallel to AB (fig. 4), and *vice versa*, the knowledge of a parallel to AB enables us to find the point M (by means of a straight-edge alone).

Fig. 4.



We can express this also by saying that with every Euclidean segment is associated a certain *characteristic point*, its mid-point, the unique image * of both the (coalescent) points $l=+\infty$ and $l=-\infty$ of the straight line AB.

We shall see that in the space of Lobatchevsky there is on every straight segment *a pair* of distinct points which take over the rôle of the mid-point. The latter is thus a double point, the coalescence of the pair.

4. *Lobatchevskyan segment.*—Let the curvature of the contemplated hyperbolic space be $K=-1/R^2$, and let us take R, a real length, as unit length. Then, our previous OUT being a straight segment in this space, we have to put in equation (2) $i=\sqrt{-1}$ instead of R. Thus the relation between the metrical and the Staudtian scales becomes

$$\text{Cot}\, l=\frac{1}{n}[\text{Cot}\, l_1+(n-1)\,\text{Cot}\, l_\infty], \quad . \quad . \quad . \quad (6)$$

where Cot stands for the hyperbolic cotangent.

Without dwelling any further upon the general relation (6), let us specialize it by taking for the Staudtian $n=1$ the metrical mid-point M of the segment. Thus, if 2λ be the total length of the segment, with R as unit, let us put $l_1=\lambda$, $l_\infty=2\lambda$. Then

$$\text{Cot}\, l=\frac{1}{n}[\text{Cot}\,\lambda+(n-1)\,\text{Cot}\, 2\lambda],$$

for any l. Solve for n and, aiming at the Lobatchevskyan

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* Or fourth harmonic of A, B, and the point at infinity, conjugate to the latter.

parallels, put $l=\infty$. Then, since $\mathrm{Tan}\,\infty=1$,

$$n=\frac{\mathrm{Tan}\,2\lambda-\mathrm{Tan}\,\lambda}{\mathrm{Tan}\,\lambda(\mathrm{Tan}\,2\lambda-1)}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Similarly, for $l=-\infty$,

$$n'=\frac{\mathrm{Tan}\,2\lambda-\mathrm{Tan}\,\lambda}{\mathrm{Tan}\,\lambda(\mathrm{Tan}\,2\lambda+1)}. \quad . \quad . \quad . \quad . \quad . \quad (7')$$

These two different indices correspond to the two "points at infinity" (or pencil centres) of the Lobatchevskyan straight line.

Remembering that $\mathrm{Tan}\,x=\dfrac{e^{2x}-1}{e^{2x}+1}$, the last formulæ are easily transformed into

$$\left.\begin{aligned} n&=-e^{+2\lambda} \\ n'&=-e^{-2\lambda} \end{aligned}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

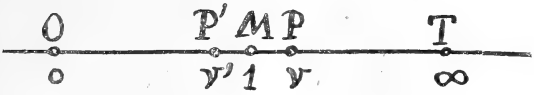
giving the simple relation

$$nn'=1. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Now, consider the two points P and P' (fig. 5), whose Staudtian indices are the negatives of those in (8),

$$\nu=e^{2\lambda}, \text{ and } \nu'=e^{-2\lambda}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Fig. 5.



In order to find their distances from the origin, $l=\overline{OP}$, and $l'=\overline{OP'}$, substitute the indices (10) into (6), with $l_\infty=2l_1=2\lambda$, as before. Then the result will be

$$\mathrm{Tan}\,l'=\frac{e^{4\lambda}-1}{1+3e^{4\lambda}}, \quad \mathrm{Tan}\,l=\frac{e^{4\lambda}-1}{3+e^{4\lambda}}. \quad . \quad . \quad . \quad . \quad (11)$$

The metrical distance $\overline{OM}$ being λ, let us find the length $\overline{P'M}=\lambda-l'$. Remembering that

$$\mathrm{Tan}\,(\lambda-l')=(\mathrm{Tan}\,\lambda-\mathrm{Tan}\,l') : (1-\mathrm{Tan}\,\lambda\,.\,\mathrm{Tan}\,l'),$$

we shall find, after easy reductions,

$$\mathrm{Tan}\,(\lambda-l')=\mathrm{Tan}^2\,\lambda.$$

And, in quite the same way, for $\overline{MP}=l-\lambda$,

$$\mathrm{Tan}\,(l-\lambda)=\mathrm{Tan}^2\,\lambda,$$

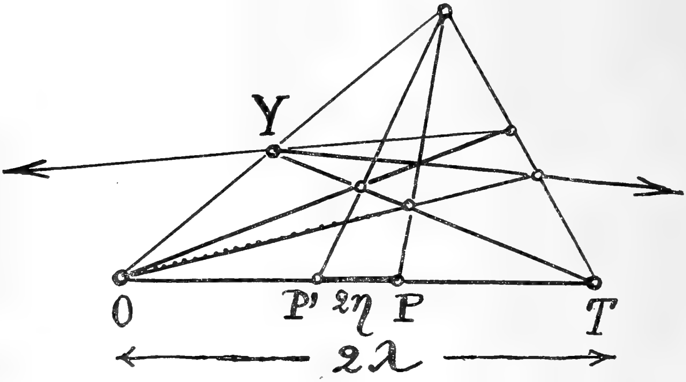
so that P and P' have a symmetrical position within the segment, as might have been expected.

Thus if the semi-length of the *gap* * $P'P$ or each of the equal distances $\overline{MP'}$, $\overline{MP}$, be denoted by η, we have the surprisingly simple result

$$\mathrm{Tan}\,\eta = \mathrm{Tan}^2\,\lambda.$$

The connexion of these two characteristic points P, P' with the Lobatchevskyan (arrowed) parallels through any point Y is shown in fig. 6, which, after what was said before, scarcely calls for further explanations.

Fig. 6.



To resume :—

Every Lobatchevskyan straight segment has intrinsically associated with it a pair of characteristic points P and P', symmetrically situated within it, whose mutual distance 2η is given by

$$\mathrm{Tan}\,\frac{\eta}{\mathrm{R}} = \mathrm{Tan}^2\,\frac{\lambda}{\mathrm{R}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and is thus a function only of the total length 2λ of the segment.

It may be interesting to notice that for segments which are small fractions of R we have, approximately, $\eta/\mathrm{R} \doteqdot (\lambda/\mathrm{R})^2$, or

$$\overline{\mathrm{PP'}} : \overline{\mathrm{OT}} \doteqdot \overline{\mathrm{OT}} : 2R, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

that is to say, the "gap" is to the whole segment as this is to twice the radius of curvature of the contemplated space.

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* This portion of the whole segment OUT deserves such a name because if the end-point X of a vector $\mathbf{X} = OX$ falls within it, there is no negative vector $-\mathbf{X}$ with O as origin. *Cf.* Proj. Vector Algebra.

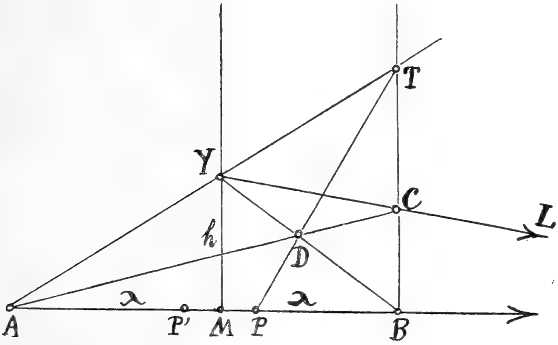
Thus if we wish to characterize palpably a particular Lobatchevskyan space, we have only to draw a segment and mark upon it the "gap" or its extremities P and P'. If we do the same thing for a pencil of equal segments from M, we have, within the circle of radius λ, a concentric circle of radius η; and similarly within a sphere of radius λ a concentric sphere of radius η determined by (12). This little sphere is an image of the inaccessible locus of "points at infinity," which is thus seen also to be a real quadric "at infinity." It is certainly agreeable to have its natural image or correlate near at hand.

If R becomes infinite, or better, if λ/R becomes smaller and smaller, the gap becomes small of the second order, until the two points coalesce into the Euclidean characteristic point, the ordinary mid-point of the segment.

5. *Verification of formula* (12).—Since some readers may find the above method based on Staudt's scale and especially our deduction of (2), not wholly convincing, it has seemed well to deduce formula (12) directly by the aid of Lobatchevskyan trigonometry or the equivalent analytic geometry, and thus to verify it *.

This can be done most easily in Weierstrass coördinates.

Fig. 7.



In fact, let the mid-point M of the given segment AB be the origin, MB and the perpendicular MY (fig. 7) the axes. Then, if N be any point of the plane and a, b, r its shortest

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* Another way of deducing (2) and (12), based on Cayley's definition of distance by the logarithm of a cross-ratio, may be left to the care of the reader.

distances from the axes MY, MB, and from the origin, respectively, the Weierstrass coördinates of N are (with $R=1$)

$$x=\operatorname{Sin} a, \quad y=\operatorname{Sin} b, \quad z=\operatorname{Cos} r,$$

satisfying the condition $x^2+y^2-z^2=-1$. All that is required for our purpose is to remember that the equation of a straight line passing through two points x_1, y_1, z_1 and x_2, y_2, z_2 is

$$\begin{vmatrix} x & y & z \\ x_1 & y_1 & z_1 \\ x_2 & y_2 & z_2 \end{vmatrix}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

and that the angle ϵ contained between any two straight lines $ax+by+cz=0$, $a'x+b'y+c'z=0$ (where $a^2+b^2-c^2=1$, etc.) is given by

$$\cos\epsilon=aa'+bb'-cc'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

It will be convenient to denote the Weierstrass coördinates x, y, z of any point N of the plane by N_1, N_2, N_3 respectively.

Since the position of the required point-pair P, P' is independent of the choice of the point Y, through which the two parallels are drawn, we may take Y on the ordinate axis, in a distance h above the origin M. Thus

$$Y_1=0, \quad Y_2=\operatorname{Sin} h, \quad Y_3=\operatorname{Cos} h.$$

The auxiliary line through the end-point B of the segment being arbitrary let us make it perpendicular to AB. In order to find the point P we have to draw through Y the right-hand parallel YL (fig. 7), *i. e.* the join of Y with the point $x, y, z=\infty, 0, \infty$. Its equation is, by (a),

$$x\mathrm{Y}_2+y\mathrm{Y}_3-z\mathrm{Y}_2=0,$$

or

$$x+y\operatorname{Cot} h=z. \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{YL})$$

The equation of the perpendicular BT is, by (a) and (b),

$$x=z\operatorname{Tan}\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{BT})$$

Thus the ratios of the coördinates of the cross $\mathrm{C}=(\mathrm{YL})(\mathrm{BT})$ are

$$\frac{\mathrm{C}_1}{\mathrm{C}_3}=\operatorname{Tan}\lambda, \quad \frac{\mathrm{C}_2}{\mathrm{C}_3}=(1-\operatorname{Tan}\lambda)\operatorname{Tan} h. \quad . \quad . \quad . \quad (\mathrm{C})$$

The equation of the join AY is

$$x\mathrm{Y}_2\mathrm{A}_3+y\mathrm{Y}_3\mathrm{A}_1=z\mathrm{A}_1\mathrm{Y}_2, \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{AY})$$

where $A_3 = \text{Cos}\,\lambda$, $A_1 = -\text{Sin}\,\lambda$. Therefore, the cross (AY) (BT) is determined by

$$\frac{T_1}{T_3} = \text{Tan}\,\lambda = \frac{C_1}{C_3}, \quad \frac{T_2}{T_3} = 2\,\text{Tan}\,h. \quad . \quad . \quad . \quad (\text{T})$$

Next, we have to find the cross D of the straight lines

$$x\,\text{Tan}\,h + y\,\text{Tan}\,\lambda = z\,\text{Tan}\,h\,.\,\text{Tan}\,\lambda, \quad . \quad . \quad (\text{BY})$$

and

$$x(1-\text{Tan}\,\lambda)\text{Tan}\,h - 2y\,\text{Tan}\,\lambda = z\,\text{Tan}\,\lambda\,\text{Tan}\,h(\text{Tan}\,\lambda - 1). \quad (\text{AC})$$

These equations give

$$\frac{D_1}{D_3} = \frac{\text{Tan}\,\lambda(1+\text{Tan}\,\lambda)}{3-\text{Tan}\,\lambda}, \quad \frac{D_2}{D_3} = \frac{2\,\text{Tan}\,h(1-\text{Tan}\,\lambda)}{3-\text{Tan}\,\lambda}. \quad (\text{D})$$

Finally, the join of D with T,

$$\begin{vmatrix} x & y & z \\ T_1 & T_2 & T_3 \\ D_1 & D_2 & D_3 \end{vmatrix} = 0,$$

gives, with $y=0$, for the abscissa $\eta = MP$ of the required point P,

$$\text{Tan}\,\eta = \left(\frac{D_1}{D_3}\frac{T_2}{T_3} - \frac{T_1}{T_3}\frac{D_2}{D_3}\right) : \left(\frac{T_2}{T_3} - \frac{D_2}{D_3}\right).$$

Substitute here the values given under (T) and (D); then the common factor $2\,\text{Tan}\,h$ will divide out, and the result will be

$$\text{Tan}\,\eta\,.\left(1 - \frac{1-\text{Tan}\,\lambda}{3-\text{Tan}\,\lambda}\right) = \frac{2\,\text{Tan}^2\,\lambda}{3-\text{Tan}\,\lambda},$$

independent of h, as was to be expected, or

$$\text{Tan}\,\eta = \text{Tan}^2\,\lambda,$$

identical with our previous result. Similarly, for the abscissa η' of the other characteristic point, the reader will find $\text{Tan}\,\eta' = -\text{Tan}^2\,\lambda$.

Thus the result, first obtained by a much simpler method, is fully corroborated.

Ryerson Laboratory, Chicago,
July 1921.

XLVII. *An Attempt to Separate the Isotopes of Chlorine.* By H. Hartley, *M.A.*, A. O. Ponder, *B.A.*, E. J. Bowen, *B.A.*, *and* T. R. Merton, *D.Sc.*, *F.R.S.*[*]

AS the isotopic elements are chemically identical, and therefore inseparable by the ordinary chemical methods of separation, there remain only physical methods of fractionation depending on small differences in the physical properties of the atoms, which, as Lindemann and Aston have shown (Phil. Mag. vol. xxxvii. p. 523, 1919), are likely to be excessively slow. It has been found, however, that the spectra of isotopes are not identical (Aronberg, Astrophys. Journ. vol. xlvii. p. 96, 1918; Merton, Proc. Roy. Soc. A. vol. xcvi. p. 388, 1920, and A. vol. c. p. 84, 1921), but that there are small differences in the wave-lengths of the principal lines in the spectra of three isotopes of lead, and probably also in the spectra of ordinary thallium and of the thallium extracted from pitchblende. In these cases the difference was established in the case of some of the strongest spectrum lines only; but since it is probable that such differences are to be found throughout the spectrum, it is of interest to consider whether they can be made of use in effecting a separation of a mixture of isotopes. Aston's (Phil. Mag. vol. xxxix. p. 620, 1920) announcement that chlorine consists of a mixture of two isotopes of atomic weights 35 and 37, with possibly a trace of another of atomic weight 39, has presented a case in which it appeared that a difference in the spectra might be turned to account (Merton and Hartley, 'Nature,' vol. cv. p. 104, 1920). Neglecting the possible isotope of atomic weight 39, it is evident that ordinary chlorine must consist of a mixture of the isotopes Cl_{35} and Cl_{37} in the ratio of very nearly 3 : 1. In the gaseous condition chlorine will thus consist, on probability considerations, of the molecules $Cl_{35}Cl_{35}$, $Cl_{35}Cl_{37}$, and $Cl_{37}Cl_{37}$ in the ratio 9 : 6 : 1. If we suppose that white light traverses a column of chlorine of such a length that the radiation absorbed by $Cl_{37}Cl_{37}$ is reduced in intensity by a factor 10^{-3}, the corresponding factors in the case of $Cl_{35}Cl_{37}$ and $Cl_{35}Cl_{35}$ will be 10^{-18} and 10^{-27} respectively. If, now, the light after passing through this column of chlorine enters a vessel containing a mixture of hydrogen and chlorine, which combine under the influence of the light absorbed by the chlorine, it would appear to follow that the initial rates of reaction for the molecules

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[*] Communicated by the Authors.

$Cl_{35}Cl_{35}$, $Cl_{35}Cl_{37}$, and $Cl_{37}Cl_{37}$ should be in the ratio $1:10^9:10^{24}$, provided that the molecules which absorb energy react at a rate proportional to the energy which they absorb and that the absorption bands do not overlap. Under these conditions the hydrochloric acid which is formed should consist almost entirely of HCl_{37}, provided that the reaction is allowed to proceed for a suitable period. Under favourable circumstances the photochemical combination of chlorine and hydrogen takes place more than a million times as fast as would be expected on Einstein's Theory of Photochemical Equivalence; and if, as seems probable from recent experiments (Nernst, *Phys. Zeit.* vol. xxi. p. 106, 1920), this is due to secondary reactions set up by the primary photochemical reactions between chlorine and hydrogen, in which large numbers of other molecules participate, it is evident that the separation of isotopes by this method would be impossible unless these secondary reactions could be eliminated.

It is also doubtful whether the difference in the spectra would be sufficient to effect a separation, as the differences which have hitherto been observed in the spectra of isotopes relate to the spectra emitted by atoms; whereas in the present case we are concerned with the absorption spectra of molecules, and there is not the smallest experimental or theoretical basis for predicting the magnitude of the difference. Account must also be taken of the widths of the absorption lines, which cannot be less than a certain inferior limit imposed by the translatory motions of the absorbing molecules, operating in accordance with Doppler's principle. Lord Rayleigh (Phil. Mag. vol. xxix. p. 274, 1915) has shown that on this basis the "half-width" $\delta\lambda$ of a line of wave-length A may be found from the equation $\frac{\delta\lambda}{\lambda}=3{\cdot}57\times10^{-7}\surd(T/M)$, where T is the absolute temperature and M the mass of the radiating or absorbing atom or molecule in terms of the hydrogen atom. In the case of absorption this equation defines the "half-width" of the absorbing power, the "half-width" $\delta\lambda$ denoting the distance in wave-length from the maximum of absorption of a line at which the absorbing power has fallen to one-half its value at the maximum. Thus in the case of chlorine molecules at 16°, for $\lambda=4000$ A we have $\delta\lambda=0{\cdot}003$ A. The relation between the absorbing power and wave-length is of the form $A_x=A_0e^{-Kx^2}$, where A_x is the absorbing power at a difference of wave-length from the maximum of absorption where the absorbing power is A_0, and K is a constant appropriate to the mass of the particles and the temperature of the gas. The absorbing power through each line can thus be plotted as a probability curve, and it is at once evident that if the maxima of absorption for the different types of molecule are at a distance apart which is comparable with the "half-widths," the effectiveness of the chlorine filter will be impaired. It can be seen, however, that the filter is still operative, though less efficient, when the difference between the maxima is less than the "half-widths" of the lines, which it would then be impossible to resolve so that they could be seen as separate lines in the spectroscope; but in the absence of any data as to the separation of the components, or their number, further discussion would be redundant.

From the foregoing considerations it is evident that, according to theory, the success of the experiment should be favoured by working at a low temperature, and that the temperature of the reaction vessel should be equal to or less than that of the filter; but the probable gain in efficiency is very small in comparison with the difficulties of manipulation at low temperatures.

Conditions for Maximum Efficiency.

By the efficiency E we denote the ratio of the number of atoms of the one kind to the number of atoms of the other kind which, in a reaction vessel one molecule in depth, combine with hydrogen to form hydrochloric acid under the influence of the light which has traversed the filter. If the chlorine contains n kinds of isotopic atoms denoted by $m_1, m_2, m_3 \ldots m_n$, in the proportion $a_1, a_2, a_3 \ldots a_n$, there will be $\frac{1}{2}n(n+1)$ kinds of molecule in the gas, and the proportions of the different kinds of molecule in the gas can be found from the coefficients of $[a_1m_1+a_2m_2+a_3m_3 \ldots +a_nm_n]^2$, where, for example, the coefficients of (m_1^2) and (m_2m_n) denote the relative numbers of the molecules (m_1, m_2) and (m_2, m_n) in the gas. In the present case we consider only two kinds of isotopic atoms which are present in the ratio $(1-x):x$, the three kinds of molecules being thus present in the ratio $(1-2x+x^2):(2x-2x^2):x^2$. If the absorption coefficient is denoted by k and the length of the column of gas in the filter by l, it can be easily shown that the efficiency

$$E = \frac{e^{-klx^2} + \frac{1}{2}e^{-kl(2x-2x^2)}}{\frac{1}{2}e^{-kl(2x-2x^2)} + e^{-kl(1-2x+x^2)}},$$

or when l is large and the second term in both the numerator and the denominator can be neglected,

$$E = 2e^{2klx-3klx^2}.$$

Differentiating and equating to zero, we find that $x=(1/3)$ for maximum efficiency when l is large, which means that if pure samples of the isotopes m_1 and m_2 were available, they should be mixed in the proportion of two parts of m_1 to one part of m_2 in order to make the most efficient filter for the separation of m_2; provided that the atoms redistribute themselves to form the molecules m_1m_1, m_1m_2, and m_2m_2 in the proportions shown above, and that the thickness of the filter were such that the proportion of light which it absorbed was large. The efficiency can, of course, be increased indefinitely by increasing the length of the filter, but a practical limit is set by the slowness of the reaction if the filter is made too long. It should be pointed out that the above calculation depends on the assumption that there is no appreciable overlapping of the absorption lines due to the different kinds of molecule. Continuous absorption superposed on the line absorption, if it were effective in promoting the reaction, would also reduce the efficiency.

Experimental.

Mixtures of hydrogen and chlorine in equivalent proportions were exposed to the action of light which had been filtered through a layer of chlorine, and after an appropriate time mercury was added to the reaction mixture to remove all the free chlorine before the mixture was exposed to unfiltered light. The remaining hydrogen and hydrogen chloride were bubbled through conductivity water, and the hydrochloric acid was converted into sodium chloride, the equivalent of which was then determined. In the first series of experiments the mixture of hydrogen and chlorine was made by the electrolysis of pure hydrochloric acid containing 30 per cent. of acid in a voltameter with arc carbons as electrodes passing through a rubber plug which was protected from the action of the chlorine by a layer of hard paraffin-wax. The mixed gases were bubbled through a wash-bottle containing 66 per cent. sulphuric acid in order to remove spray and hydrogen-chloride vapour. The gases then passed into the reaction vessel of 1850 c.c. capacity which had been previously exhausted by means of a Gaede rotary oil-pump to a pressure of about 0·3 mm. When the reaction vessel had been filled to atmospheric pressure, it was cut off from the voltameter and enclosed in a light-tight box provided with suitable aperture and exposed to the rays from a "half-watt" lamp which had been made parallel by a lens and had passed through a chlorine filter half a metre in length and 2 cm. in diameter. After an appropriate exposure, dry mercury was run into the reaction vessel by means of a tap funnel sealed on to it, and the vessel was shaken until the absorption of chlorine by the mercury was complete. The remaining hydrogen chloride was then washed out of the reaction vessel by a current of pure air and absorbed in conductivity water. The concentration of the hydrogen chloride in solution was then determined by conductivity measurements.

In a second series of experiments the mixture of hydrogen and chlorine was dried by passage through a second wash-bottle containing 98 per cent. sulphuric acid, and the rate of reaction was increased by using three half-watt lamps and filtering the light through two large flasks of chlorine which were provided with stops so as to give an effective aperture of about 10 cm. and a thickness of 50 cm.

In these experiments the reaction vessel was not cut down from the voltameter each time, and the hydrogen chloride was separated by drawing the reaction mixture into a large vacuous vessel containing mercury, which was attached by means of a ground-joint.

The amounts of hydrogen chloride obtained and the percentage conversion of the mixture in each experiment were as follows :—

Series 1.

No. of experiment.	Percentage conversion of mixture.	Yield of hydrogen chloride.	Period of exposure.
1 …………	5·0	0·15 gram.	18 hours.
2 …………	2·8	0·086 ,,	48 ,,
3 …………	3·7	0·11 ,,	48 ,,
4 …………	3·8	0·12 ,,	48 ,,
5 …………	5·2	0·15 ,,	48 ,,
6 …………	11·6	0·36 ,,	48 ,,
7 …………	2·2	0·068 ,,	18 ,,

Series 2.

No. of experiment.	Percentage conversion of mixture.	Yield of hydrogen chloride.	Period of exposure.
1 …………	6·0	0·235 gram.	15 hours.
2 …………	6·75	0·264 ,,	12½ ,,
3 …………	6·75	0·264 ,,	9½ ,,
4 …………	6·2	0·242 ,,	8 ,,
5 …………	7·4	0·288 ,,	7¾ ,,

Determination of the Equivalent of the Chlorine.

The hydrogen chloride was converted into sodium chloride by neutralization with sodium carbonate, and the equivalent of the chlorine was determined by converting it to silver chloride and determining the end-point of the reaction by the nephelometer. The first experiments indicated that a partial separation had taken place; but as the amount of sodium chloride was insufficient to admit of recrystallization, and the presence of any impurities would have given too high a value for the equivalent of chlorine, the value was very kindly redetermined by Mrs. D. L. Chapman in a specimen of silver chloride which was thought to contain an excess of the higher isotope, by reducing a known weight in a current of hydrogen and weighing the silver produced, thus eliminating the effect of any impurities originally present in the sodium chloride. The first determination gave the value 35·458, and the hydrogen chloride obtained in the reduction after reconversion to silver chloride gave the value 35·461 in a second determination. These figures agree so closely with the standard value for the equivalent of chlorine (35·46) that it is clear that no separation had taken place within the limits of experimental error. This was confirmed by preparing some hydrogen chloride in the same apparatus with unfiltered light, and determining the equivalent of the chlorine by the nephelometric method. A value 35·59 was found, agreeing almost exactly with two values found for hydrogen chloride prepared with filtered light (35·59 and 35·58), thus showing that, in spite of the precautions, the sodium chloride contained about 0·1 per cent. of impurity.

It is impossible to say whether the failure to effect a separation is due to the secondary reactions mentioned above or to the difference in the absorption spectra of the two isotopes being insufficient for the purpose; and it is hoped to investigate this further by applying the method to the chlorination of substances similar to monobromtrichlormethane, in which case Noddack has found that the secondary reactions do not occur (*Zeit. für Elektrochemie*, vol. xxvii. p. 359, 1921).

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XLVIII. *Latent Heats of Fusion.—Part I. Benzophenone, Phenol, and Sulphur.* By Mrs. K. STRATTON, *M.Sc.*, *and* Prof. J. R. PARTINGTON, *D.Sc.**

THE determination of the latent heat of fusion of a substance has been carried out in one of two ways:—(1) Calorimetrically, (2) Indirectly from van't Hoff's equation: $E=0{\cdot}02T^2/L$, where E = molecular depression of the freezing-point for 100 grams of solvent; L = latent heat of fusion of substance in gram calories per gram; T = melting-point (absolute).

No systematic investigation of Latent Heats of Fusion seems to have been made; the nearest approach is a classical research of J. F. Eykmann †, to which frequent reference is made by later experimenters. Eykmann's results, however, were all found indirectly from the Molecular Depressions of Freezing Point by means of van't Hoff's equation, and an inspection of some series of values reveals very large discrepancies between different experiments. These apparently can be explained only on the assumption that the materials used were not pure, or that the errors of experiment were unduly large. The first supposition is confirmed by Eykmann's results for phenol. Two samples of phenol were used, the melting-points being given as 36° C. and 39° C. respectively, whilst the melting-point of pure phenol we find to be 41°·5 C. In no case does Eykmann discuss in detail the purity of his materials, and it can hardly be questioned that the whole of his results fall far short of the accuracy which may be attained. This method, apart from its indirect character, did not appear to us suitable for the object we had in view. It is also not at all certain that the addition of a second substance may not modify, to an unknown extent, the molecular constitution of the first in the liquid state. A comparison of the values of the latent heat determined, with the same degree of accuracy, by the direct and indirect methods is expected to throw light on this question.

The direct calorimetric methods, as applied by former experimenters ‡, although simple in execution, involve a knowledge of additional data which is not always available. Apart from the somewhat large cooling corrections for the calorimeter, it is necessary to know the specific heats of the

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* Communicated by the Authors.

† *Zeitschr. physikal. Chem.* iv. p. 497 (1889).

‡ Person, *Annales de Chimie*, xxx. p. 73 (1850); Bruner, *Ber.* vol. xi. p. 2102 (1894); Battelli, *Att. Accad. Lincei*, p. 621 (1885).

solid and liquid substances and the exact melting-point. None of these magnitudes is required in the method described in the present communication. The principle of the method used is simple. To a known weight W grms. of the solid, maintained accurately at its melting-point, a measured amount of heat is imparted by a wire of resistance R ohms heated by a uniform current of C amperes. This heating is carried out under such conditions that no transfer of heat between the system and its environment is possible. If the time required to bring about complete fusion under these conditions is t seconds, we have without any corrections

$$L = C^2Rt/4{\cdot}18\ W \text{ grm. cal. per gram.}$$

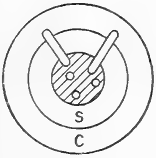
Apparatus.

A weighed amount of the substance was placed in an inner vessel A (fig. 2), surrounded by an outer vessel B containing the same substance, partly in the molten condition and therefore at its melting-point. The outer vessel itself was surrounded by a heat insulating arrangement which served to prevent undue loss of heat from the bath B during the course of the experiment, which would lead to solidification of the material. The inner vessel A was a small glass beaker, capacity 80 c.c. The outer vessel B was an enamelled iron pot, capacity 750 c.c.

The heat insulating arrangement in the earlier experiments was a wooden box containing hay and cotton-wool.

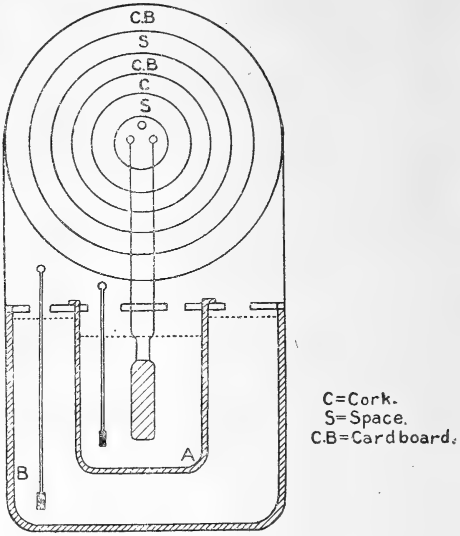
The inner vessel A was provided with a cork, cut so that the solid centre provided a support for the heating coil (see fig. 1). The centre piece also had two small holes to allow the passage of the copper leads of the coil. With this arrangement it was possible to use the heating coil to some extent as a stirrer during the experiment. The outer rim of the cork, from which the solid centre piece was suspended, was cut so that a thermometer acting as a combined recorder of temperature and a stirrer could be placed in the midst of

Fig. 1.



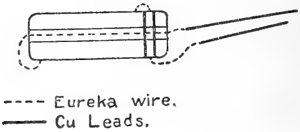
the substance in the vessel A (see figs. 1 and 2). The outer enamelled pot was fitted with a cardboard top, the cardboard $\frac{3}{8}$ of an inch thick, through which the inner vessel could be suspended in the molten substance in B. The cardboard was cut to allow the passage of a thermometer into the bath, this again acting as a temperature recorder and stirrer.

Fig. 2.



The heating coil was made in the following way :—A piece of ebonite rod, 3 cms. in length, 0·75 cm. in diameter, was taken, and a small hole drilled through its length. A small hole was also drilled from side to side at one end (see fig. 3);

Fig. 3.



a thin groove was turned on the rod to keep the coiled wire in position. One end of the Eureka wire of 0·3 mm. diameter was threaded through the hole in the top, wound round the rod, then at the opposite end was drawn through the centre of the rod and out at the farther end. The holes were then plugged up with small pieces of ebonite, so that the coil was solid and compact and there was no fear of the wire short-circuiting. (See fig. 3 for section of coil.)

The ends of the Eureka wire were soldered on to fairly thick copper leads, 0·75 mm. diameter. The current was provided in the earlier experiments by accumulators; in later experiments these have been replaced by current taken directly from the 240 volt mains by using a large lamp resistance. The current passed through a calibrated ammeter and the whole circuit connected through a sliding resistance and a plug key for convenience.

Method of Experiment.

A weighed amount of the pure dry solid in powder or small pieces was placed in the inner vessel. The heating coil was placed in the centre and the thermometer embedded in the solid. The inner vessel was then suspended in the bath, this being kept exactly at the melting-point by having some unfused solid present and by keeping the whole well stirred. The whole apparatus was then placed in the hay-box and the spaces in the cardboard and cork lids kept covered as much as possible by cotton-wool to prevent loss of heat. The temperature of the solid in the inner vessel gradually rose until it attained the melting-point. It was allowed to remain at this temperature for at least 15 minutes to make sure that all the solid was at the same temperature. This was tested by moving the thermometer about in the solid.

The heating coil was then connected in circuit and current passed through, the solid in the inner vessel being kept vigorously stirred and the heating coil moved backwards and forwards to ensure even heating. When all the solid had fused the temperature began to rise; the time at this stage was noted, as this corresponds with the time t, during which heat is supplied for fusion of the substance. The current throughout the experiment registered by the ammeter was also noted.

Results.

I. *Benzophenone.*—This was purified by recrystallization from light petroleum, the resulting product was in the form of white needles, M.P. 48° C. For the loan of one specimen of Benzophenone we are indebted to Prof. J. N. Collie. A beaker was in this case used as the outer heating vessel.

1*st Experiment.*—Wt. of Benzophenone=35·660 grms. =W.; Time of passage of current=17 mins. 30 secs.=*t*; Current strength=0·85 amp.=C; Resistance of coil=4·25 ohms=R. ∴ $L=C^2Rt/4{\cdot}18W=21{\cdot}64$ gram cal.

2*nd Experiment.*—C=1·48 amps.; Wt. of Benzophenone =31·135 grms.; R=(a new coil used here) 1·33 ohms; *t*=15 mins. ∴ L=21·79 gram cal.

3*rd Experiment.*—C= 1·08 amps.; R = 1·33 ohms; *t*=28 mins. 58 secs.; Wt. of Benzophenone=29·757 grms. ∴ L=21·58 gram cal.

From these results we may calculate the value of the Molecular Depression of the Freezing Point from formula $E={\cdot}02T^2/LW$.

For L=21·64,	E=95·11
For L=21·79,	E=94·61
For L=21·68,	E=95·04
Mean L=21·70,	Mean E=94·92

The values quoted by Nernst (*Theoretische Chemie*, 7 Aufl. p. 149, 1913) are L=21·5 (observed) and E=95 (obs.); E=96 (calculated from L).

The authority given by Nernst for these values is Eykmann. The observed values of E given in Eykmann's paper, however, range between 68 and 100. It might also be noted here that the values given by Eykmann for phenol are arranged under two headings: those for phenol with a M.P. 36° C., and those for a phenol of M.P. 39° C. These results are unreliable for obvious reasons.

In the monograph *Cryoscopie*, by Raoult, 1901, page 70, a table is given of values derived from the constant E. This is divided by the molecular weight of the solvent, giving a constant which represents the lowering of the freezing-point produced by dissolving 1 gram molecule of the solute in 100 grms. of the solvent expressed in gram molecules, which constant it is stated should be in the neighbourhood of 0·62.

The value Raoult gives for this constant for Benzophenone is 0·54; the value for the mean of our experimental results is 0·522. The value for E, therefore, used by Raoult from the work of Eykmann, to which he refers, is 98·28, differing considerably from the value used by Nernst for a different purpose.

In Landolt and Börnstein's *Tabellen*, the values of L for Benzophenone are given as 23·7 (Bruner, *Ber.* ii. p. 2102, 1894), and 23·4 (Tammann, *Zeit. physikal. Chem.* xxix. p. 64, 1899). Bruner's value is stated by him to be in "sufficient" agreement with the value 21·5 determined from the value of E, quoted by Nernst from the paper of Eykmann. We refer to these points in order that a comparison may be instituted between the accuracy attained in previous researches and that of the present preliminary experiments. It will be seen that such a comparison is very favourable to the latter.

Experiments with Phenol.

The phenol was purified by distillation ; the product used, which was perfectly white, had a B.P. 181° C. and M.P. 41°·5 C.

1*st Experiment.*—$R=2{\cdot}80$ ohms ; $C=1{\cdot}08$ amps. ; time $t=47{\cdot}95$ mins. ; $W=77{\cdot}357$ grms. $\therefore$ $L=28{\cdot}93$ gram cal.
2*nd Experiment.*—$R=2{\cdot}80$ ohms ; $C=0{\cdot}74$ amp. ; time $t=119$ mins. ; $W=89{\cdot}29$ grms. $\therefore$ $L=29{\cdot}2$ gram. cal.

These values of L do not agree with the value given by Nernst in the table previously referred to, and consequently do not agree with the values calculated in Eykmann's paper ; the latter gives $L=25$.

Owing to the large value of t used in the two experiments quoted above there is a possibility of the determined value of L being somewhat too large, although we are not inclined to think that 25 cal. is the correct value. We hope, therefore, to repeat the determinations for phenol with greater accuracy at a later date. Some improvements in the experimental method are also being worked out.

Experiments with Sulphur.

It was originally intended to carry out experiments with both monoclinic and rhombic sulphur, so as to enable us to calculate the heat of transition from the values of L for these two substances. The attempts to find the latent heat of rhombic sulphur were not successful, because during the time required to get the sulphur in the inner and outer vessels at the same temperature the transition from rhombic to monoclinic sulphur took place rapidly.

The sulphur used was recrystallized from toluene.

This sulphur was placed in the outer bath, heated to 130° C. and kept as nearly as possible at this temperature for two hours. It was then cooled and began to solidify at 120° C. It was kept at this temperature by being surrounded with a second outer bath of paraffin-wax, kept as nearly as possible at 120° C.; the presence of both the solid monoclinic form and liquid in the sulphur bath prevented variations in temperature.

A weighed amount of pure sulphur was then placed in the inner vessel, and this placed in the sulphur bath after being previously heated on a water bath for 2 hours. The temperature of this gradually rose to 120° C. and was allowed to remain at this temperature for at least half an hour. The coil was then connected up and the sulphur fused. The coil used in these experiments was a little different from those used for phenol and benzophenone. It was thought that the sulphur when heated might attack the ebonite, so that thick mica was substituted, a flat piece, rectangular in shape, 1 inch long, $\frac{3}{4}$ inch wide, and $\frac{1}{8}$ inch thick, being used for supporting the coil.

Results.

1*st Experiment.*—$W=47{\cdot}7094$ grms.; $C=1{\cdot}43$ amps.; $R=2{\cdot}56$ ohms; $t=5$ mins. 40 secs. $\therefore L=8{\cdot}87$ gram cal.

2*nd Experiment.*—$W=46{\cdot}0434$ grms.; $C=1{\cdot}38$ amps.; $R=2{\cdot}56$ ohms; $t=5$ mins. 50 secs. $\therefore L=8{\cdot}82$ gram cal.

These results do not agree with the value for monoclinic sulphur given by Wigand (*Zeit. physikal. Chemie*, lxiii. p. 273, 1908), viz.

$$L=10{\cdot}4 \text{ grm. cal. per grm. (monoclinic).}$$

The sulphur experiments, it is also hoped, may be repeated. An improvement would be to convert the sulphur mainly to the monoclinic form before the experiment. It may be noted, however, that the presence of unconverted rhombic sulphur would, according to Wigand's data, have raised the value of L, which in our experiments is lower than that found by Wigand. By using smaller quantities of material we think it will be possible to determine the latent heat of rhombic sulphur. Any error in our method would appear to make a *high* result probable, whereas our values are somewhat *lower* than those of previous experimenters when any appreciable difference exists.

Summary of Experimental Results.

The results so far obtained may be summarized as follows:—The latent heats of fusion in gram calories per gram of substance are: benzophenone 21·70; phenol 29·06; monoclinic sulphur 8·85. The probable accuracy is greatest for the benzophenone.

Theoretical Considerations.

Although the thermal properties of the solid state may now be regarded as fairly satisfactorily established, the liquid state is still in many respects obscure. This uncertainty is reflected in the difficulty which at present exists of forming any definite conception of the molecular changes which accompany fusion, and it is not surprising that the relations between the energy-changes on fusion and the molecular properties of the materials are almost entirely empirical. In the case of evaporation, the well-known rule of Trouton, $ML/T = \text{const.} = 21$ ($M =$ molecular weight) is known to hold fairly accurately for non-associated liquids.

P. W. Robertson (Trans. Chem. Soc. lxxxi. p. 1233, 1902) suggested the expression $ML/T\sqrt[3]{V} = \text{const.}$, where L is the latent heat of fusion, T the melting-point (absolute), and V the molecular volume. In the case of monatomic metals ($M > 40$) the constant is 1·13; inorganic salts gave a mean constant of 2·0; organic compounds, 2·2–3·0. It is known that the boiling-point is a "corresponding temperature" in the theory of corresponding states (see Partington, 'Thermodynamics,' p. 234); if T_c and T_m are the critical temperature and melting-point of a substance, then, according to F. W. Clarke (Amer. Chem. J. xviii. p. 618, 1896), $T_c/T_m = 2$, so that fusion is also a "corresponding state." E. Mathias (*Le point critique*, p. 59, 1904), on the assumption of the law of the rectilinear diameter, also deduces that T_m is a corresponding temperature, and the same assumption is made by V. Kourbatow (*J. Chim. Phys.* vi. p. 339, 1908). P. Walden (*Zeitschr. Elektrochem.* xiv. p. 713, 1908) assumes that the relation $M/T = \text{const.}$ holds for the fusion of non-associated substances, the value of the constant for 35 organic substances being 13·5 (12·1 to 14·2). For other substances the "degree of association," x, is assumed to be given by $13{\cdot}5\Big/\frac{ML}{T}$. Benzophenone, betol, and anthracene, for example, are assumed to be normal; formic and acetic acids, phenol, and benzene have association factors less than 2.

E. Baud (*Comptes rendus*, 152, p. 1480, 1911) proposes the equation $L = k(v_l - v_s)$, where v_l and v_s are the specific volumes of the liquid and solid at the melting-point. According to G. Tammann (*Krystallisieren und Schmelzen*, p. 41, 1903), the constant k is the absolute melting point T_m. J. Narbutt (*Zeitschr. Elektrochem.* xxv. pp. 51, 57, 1919) finds large discrepancies in the application of Tammann's formula; Walden's rule gives fairly satisfactory results if different constants are used for ortho-, meta-, and para-compounds. The value of k in Baud's formula, for 1 gram molecule, Narbutt gives as 272·5. Narbutt attempts to apply the Nernst-Lindemann formula, the frequency being calculated by Koref's rule (see Partington, 'Thermodynamics,' pp. 527, 530), but with unsatisfactory results.

H. G. Wayling (Phil. Mag. xxxvii. p. 495, 1919) proposes the rule $nL/T_m=N$; in this equation N=number of atoms in molecule, n is the "molecular number," *i. e.* the sum of the atomic numbers of the atoms in the compound (H. S. Allen, Trans. Chem. Soc. cxiii. p. 389, 1918). In the case of salts containing water of crystallization, and in the few organic compounds considered (except formic acid and chloroform), this rule breaks down.

The most attractive theoretical investigation we have met with is that of K. Honda (Sci. Rep. Tohuku Imp. Univ. vii. p. 123, 1918), which is based on the quantum theory. The atoms or molecules in the solid are allocated an amount of

$$\text{energy}\quad \epsilon=h\nu\Big/\left(e^{\frac{h\nu}{kT}}-1\right)=k\beta\Big/\left(e^{\frac{\beta\nu}{T}}-1\right),\ \text{or}\ R\beta\Big/\left(e^{\frac{\beta\nu}{T}}-1\right)$$

per gram molecule. The constants h and k are Planck's constant and Boltzmann's constant, respectively, $\beta=h/k$ is an absolute constant $=4{\cdot}863\times10^{-11}$, and $R=N_0k$ is the gas constant per gram molecule. Rotational energy in the solid is assumed to be small, except at very high temperatures. The molecules set free on liquefaction are assumed to retain the energy referred to, but to acquire also rotational energy corresponding with 2 or 3 degrees of freedom, the energy per degree of freedom being $\frac{1}{2}\epsilon$. The total energy acquired on fusion will then be, per gram-molecule, $N_0\epsilon=E$ or $\frac{3}{2}E$, according as the liquid molecules have an axis of symmetry or not. Thus $ML=\frac{1}{2}nE$, where $n=2$ or 3. The value of E is calculated by Einstein's formula (given above) with a value of ν, the frequency, given by Lindemann's equation:

$$\nu=3{\cdot}08\times10^{12}\sqrt{\frac{T_m}{MV^{\frac{2}{3}}}}.$$

This formula is applied both to elements and compounds, and it is noteworthy that although n is 2 in the case of many elements, the value 3 is also required for some elements (*e. g.* zinc) usually assumed to be monatomic. Honda obtains a fairly satisfactory agreement for a number of elements and compounds, although in some of the latter values of n much higher than 3 have to be assumed (*e. g.* 6 for KF, 7 for $PbCl_2$).

It is to be expected on theoretical grounds that the energy content of molecules at the fairly high temperatures of fusion would be more satisfactorily given by the formula of Debye than that of Einstein (see Partington, 'Thermodynamics,' p. 535; Jeans, 'Dynamical Theory of Gases,' 2nd edit. p. 422). On Debye's theory the energy content E corresponding with three degrees of freedom is given per gram molecule by

$$E=\tfrac{3}{4}RT\left[\frac{C}{C_\infty}+\frac{3\beta\nu/T}{e^{\frac{\beta\nu}{T}}-1}\right].$$

The values of E/T for given values of $\beta\nu/T$ are tabulated by Nernst (*Grundlagen des neuen Wärmesatzes*, p. 206, 1918), and greatly facilitate the calculations. The values of E/T taken from these tables may be regarded as giving the values of $3E_f/T$, where E_f is the energy per degree of freedom for rotation. A comparison of $E_f/2T$ with ML/2T (observed) will then give the value of n, the number of degrees of freedom of rotation it is necessary to assume for the liquid molecule.

The following example will illustrate the method of calculation :—

Benzophenone.—M=182. $T_m=321$. d (density)=1·098.

∴ ν from Lindemann's formula $=0·7447\times10^{12}$.

∴ $\beta\nu=36·2$. ∴ $\beta\nu/T_m=·1128$.

Value of $3E_f/T_m$ corresponding with $\beta\nu/T$ = from Tables =5·709. Observed $ML/T_m=12·28=nE_f/2T_m=12·28$.

∴ $n=12·9$. This, it will be observed, is much higher than any value recorded by Honda. This example also serves to bring out the complete failure of Wayling's rule: "molecular number" of benzophenone=96. ∴ $nL/T_m=6·5$, whereas the number of atoms in the molecule is 24.

In the table are given the values of $E_f/2T_m$ calculated by Debye's formula, with the values of ML/T_m from the experimental results of various investigators. For convenience in applying other quantum formulæ the values of $\beta\nu$ from Lindemann's formula are also included. It will be seen that for many elements and simple compounds the modified theory of Honda which has been proposed is fairly satisfactory, although in some cases the interpretation of values of n greater than 3 is not yet clear. It is possible that the large values of n represent intramolecular vibrations; at least it seems to be that complicated molecules, in which the possibility of intramolecular vibration is greater (as is known from the values of $\gamma = C_p/C_v$ in the case of gases and vapours), have high values of n. It is proposed to return to this question in a further communication.

Table I.

Substance.	M.	ML obs.	T_m.	$\nu \times 10^{-12}$.	$\beta\nu$.	$\frac{E_f}{2T_m}$.	$\frac{ML}{T_m}$.	n.
Hydrogen	2	16	14	2·669	129·8	0·0247	1·14	4·6
Nitrogen	28	192	62·5	1·402	68·17	0·645	3·07	4·8
Chlorine	70	814	169·5	1·578	76·72	0·835	4·790	5·7
Mercury	200	550	234·3	1·361	61·19	0·89	2·34	2·6
Bromine	159·8	1293	265·7	1·069	51·95	0·99	4·879	5
Iodine	254	1487	386·5	1·023	49·75	0·944	3 84	4
Potassium	39	574	336·5	2·53	123	0·875	1·71	1·9
Sodium	23	626	371	2·921	142·1	0·86	1·68	1·9
Lead.................	207	1118	600	1·99	96·8	0·934	1·86	2·0
Sodium hydroxide.	40	1610	633	4·601	223·8	0·868	2·543	2·9
Potassium fluoride.	58	6275	1133	4·737	230·3	0·92	5·525	6·0
Silver bromide ...	187	2370	703	1·92	93·4	0 945	1·89	2·0
Lead chloride	178	5150	764	1·40	65·1	0·955	6·67	7·0
Barium chloride..	208·3	5581	1232	1·900	92·39	0·96	4·471	4·7
Acetic acid	60·03	2641	289·7	1·757	85·43	0·888	10·91	12·3
Phenol	94	2735	313	1·261	61·31	0 923	7·49	8·1
Benzene	78	2340	278·5	1·306	63·5	0·909	8·5	9·4
Benzophenone......	182	3950	321	0·7447	36·20	0·9515	12·28	12·9
Naphthalene	128·1	4483·5	353	1·064	51·71	0·941	12·70	13·5

Summary.

The latent heats of fusion of benzophenone (21·70 g. cal. per g); phenol (29·06 g. cal. per g.); and monoclinic sulphur (8·85 g. cal. per g.) have been determined by electrical heating at the melting-point. A theory of fusion from the point of view of the quantum theory, with the use of Debye's formula for the energy, has been suggested. In some cases the existence of intramolecular vibrations, as well as rotations, is shown to be probable in the case of liquid molecules.

The authors desire to express their thanks to the Chemical Society for a grant which largely covered the expense of the investigation.

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XLIX. *On the Convection of Light (Fizeau Effect) in Moving Gases.* By C. V. Raman, *M.A., Hon. D.Sc., Palit Professor of Physics in the Calcutta University, and* Nihal Karan Sethi, *D.Sc.**

[Plates VI. & VII.]

1. *Introduction.*

It was early in the last century that Arago tried his famous experiment with the prism to detect whether the æther in the interior of a material body and the light-waves travelling inside it are carried along with that body in its motion, and it was to explain the negative result of this experiment that Fresnel propounded his well-known hypothesis that the æther outside a moving body remains stationary while that inside it drifts along with it, though with a diminished velocity. He deduced a law according to which this diminished velocity is given by the relation

$$u' = \left(1 - \frac{1}{\mu^2}\right) u,$$

where u is the velocity of the body and μ its refractive index. This result also explained why the aberration of the fixed stars was found by Airy and Hoek to be independent of the nature of the substance filling the telescope tube. And on account of its fundamental importance in the theory of Optics, some of the most eminent physicists have devoted considerable energy to verifying the different aspects of this law. More recently it has gained additional importance on account of the fact that this law follows as a matter of course from Einstein's remarkable principle of the relativity of space and time †, and its experimental verification is now looked upon as one of the proofs of the correctness of his theorem of the addition of velocities and consequently of the special Principle of Relativity.

We are, in the present note, not concerned with the first part of Fresnel's law, which demands a fixity of the æther outside a moving body and which found support in the experiments of Sir O. Lodge ‡, who failed to discover a drift of æther in the neighbourhood of moving matter, even in the narrow space between two revolving disks or a crevice in a massive sphere. The apparent disagreement of these

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* Communicated by the Authors.

† See Cunningham's 'Theory of Relativity,' p. 61.

‡ Phil. Trans. A, 1893, p. 727.

with the experiments of Michelson and Morley [*], which seem to contradict this fixity of the external æther, has been explained away by FitzGerald and Lorentz as being due to an inevitable change in the dimensions of the apparatus on account of its motion with the earth, an explanation very considerably simplified and made almost self-evident by the advent of the Relativity Principle [†].

But so far as the second part is concerned, the only evidence of a positive character in favour of this law of æther drift was furnished by the celebrated experiments of Fizeau, in which a delicate interference method was employed to detect and measure a change in the velocity of light on account of a velocity of about 7 metres per second of a column of water through which it was made to travel. This experiment was repeated by Michelson and Morley [‡] in 1886 with improved apparatus, and it demonstrated the surprisingly good agreement with theory. But the appearance of the elaborate electron theory of Lorentz made this agreement much less brilliant; for he showed that in dispersive media the convection coefficient was not $1-\frac{1}{\mu^2}$, but $1-\frac{1}{\mu^2}-\frac{\mathrm{T}}{\mu}\cdot\frac{d\mu}{d\mathrm{T}}$. This necessitated a more careful repetition of the experiment which has recently been accomplished by Zeeman [§], and the result is decidedly in favour of the new theory. The subject has been further followed up by him, and he has succeeded in overcoming the enormous experimental difficulties, and has actually determined for glass and quartz not only the Fresnel coefficient, but also the Lorentz correction for dispersion.

In view of this recent work and the accuracy which has been attained in the measurements, it is hardly necessary to refer to the work of Sir J. J. Thomson [‖], which led to the result that an electromagnetic wave inside a moving body should drift with half the velocity of that body. In support of this, it was argued that the substances for which Fresnel's law was actually verified in a positive manner happened to be such that $1-\frac{1}{\mu^2}$ was in their case very nearly equal to $\frac{1}{2}$. But even before the work of Zeeman, it was quite evident from the negative results of the experiments with

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[*] Phil. Mag. 1887, p. 449.

[†] Cunningham, 'Relativity and Electron Theory,' p. 34.

[‡] Amer. Journ. of Science, xxxi. p. 377 (1886).

[§] *K. Akad. Amst. Proc.* xvii. p. 445 (1914); xviii. p. 398 (1915); xxii. pp. 462 & 512 (1920).

[‖] Phil. Mag. April 1880.

moving air conducted by Michelson and Morley that Thomson's value for the convection coefficient could not be correct.

While, therefore, all the available evidence is strongly in favour of Fresnel's value or, rather, Lorentz's corrected value, at least in the case of solids and liquids, it is highly desirable that it should be confirmed in the case of gases also. A special grant secured from the Calcutta University through the kind offices of Sir Asutosh Mookerjee has enabled the writers to undertake this research, and it is proposed to give here a preliminary account of the progress of the work and of the difficulties encountered.

But before we do so it might be of interest to deduce Fresnel's law for gases from slightly different considerations. The late Lord Rayleigh[*] in discussing the scattering of light by small particles and in referring the blue colour of the sky to the molecules of air, deduced an expression for the refractive index of the gas in terms of the molecular constants. Following the same line of argument, we may also deduce on Doppler's Principle an expression for the altered refractive index when the air molecules are set in motion with a constant velocity v in a definite direction. On this principle, the incident light of wave-length λ is received by the molecules as light of wave-length

$$\frac{1}{1-\frac{v}{b}},$$

where b is the velocity of light in the medium without these scattering molecules. Thus, in the notation of Lord Rayleigh, the expression for the vibration scattered from the molecule in a direction making an angle θ with that of the primary vibration is

$$\frac{D'-D}{D}\cdot\frac{\pi T}{r\lambda^2}\left(1-\frac{v}{b}\right)^2\sin\theta\cos\frac{2\pi}{\lambda}\left(bt-r\right).$$

And considering the particles which occupy a thin stratum dx perpendicular to the primary ray x, the resultant, at a point on the incident ray, of all the secondary vibrations which issue from this stratum is

$$n\,dx\int_x^\infty\frac{D'-D}{D}\cdot\frac{\pi T}{r\lambda^2}\left(1-\frac{v}{b}\right)^2\cos\frac{2\pi}{\lambda}\left(bt-r\right)2\pi r\,dr$$

$$=n\,dx\frac{D'-D}{D}\cdot\frac{\pi T}{\lambda}\left(1-\frac{2v}{b}\right)\sin\frac{2\pi}{\lambda}\left(bt-x\right).$$

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[*] Sc. Papers, vol. iv. p. 395.

This, combined with the primary wave $\cos\frac{2\pi}{\lambda}\left(bt-x\right)$, will give $\cos\frac{2\pi}{\lambda}\left(bt-x-\delta'\right)$, where

$$\delta'=n\mathrm{T}\,dx\frac{\mathrm{D}'-\mathrm{D}}{2\mathrm{D}}\left(1-\frac{2v}{b}\right).$$

If μ' be the effective refractive index of the medium as modified by the moving molecules, that of the medium without the particles being taken as unity,

$$\delta'=(\mu'-1)\,dx.$$

And therefore

$$\mu'-1=n\mathrm{T}\frac{\mathrm{D}'-\mathrm{D}}{2\mathrm{D}}\left(1-\frac{2v}{b}\right).$$

But it has been shown by Lord Rayleigh that if μ be the refractive index with the molecules when they do not have the velocity v,

$$\mu-1=n\mathrm{T}\frac{\mathrm{D}'-\mathrm{D}}{2\mathrm{D}};$$

$$\therefore\quad \mu'-1=(\mu-1)\left(1-\frac{2v}{b}\right);$$

$$i.\,e.,\quad \mu-\mu'=2(\mu-1)\frac{v}{b},$$

which, in terms of the corresponding velocities of light V and V′, reduces to

$$\mathrm{V}'-\mathrm{V}=v\,.\,\frac{2(\mu-1)}{\mu^2}\,.$$

In the case when μ does not much differ from 1, as in air, this becomes

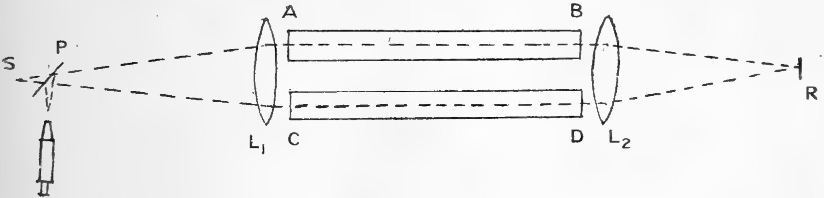
$$\mathrm{V}'-\mathrm{V}=v\frac{(\mu+1)(\mu-1)}{\mu^2}\quad[\text{since }\ \mu+1=2]$$

$$=v\left(1-\frac{1}{\mu^2}\right).$$

2. *Experimental Methods.*

It was proposed to employ the same optical arrangements as had been used by Fizeau and which constitute in effect a compensated Rayleigh Interferometer, and which are eminently suited for this work. Michelson's arrangement might have been better, but owing to the great length of path necessary, the attempt to observe the fringes with it did not prove to be a success. A large refracting telescope with a 7 inch object-glass and a focal length of over 7 feet was available from the observatory of the Indian Association for the Cultivation of Science, and was made use of in the work. The plan of the optical arrangement is shown in fig. 1, from

Fig. 1.



which it is clear that if l be the length of each of the tubes AB and CD, the shift of the fringes observed when a current of air is sent round with a velocity v in the direction of the arrows will be

$$\frac{4lv\theta}{\lambda V}$$

of the distance between two consecutive maxima or minima, where θ is the convection coefficient and V is the velocity of light in the medium. If, however, the current is first allowed to flow as in the figure and then suddenly reversed, the total shift will be double this or equal to $\frac{8lv\theta}{\lambda V}$. It is evident, therefore, that what is required in order to increase the shift and render it measurable is that both l and v should be increased. Consequently we proposed to utilize all the space available to us and make the tubes about 200 feet in length. For driving the current it was proposed to utilize a Pressure Blower driven by a 3-h.p. gas engine (fig. 3, Pl. VI.). With this we expected a velocity of air of over 50 metres per sec. in the tubes. The amount of shift of the fringes which we could therefore expect became

$$\frac{8\times 200\times 30\times 5000\times\left(1-\frac{1}{(1\cdot 0003)^2}\right)}{5\times 10^{-5}\times 3\times 10^{10}},$$

or about one-tenth of a fringe-width, which should be easily measurable with sufficient accuracy. In Michelson and

Morley's experiment the size of the apparatus was very much smaller and the velocity of air not more than about 25 metres per sec., so that the observed shift was, as stated by them, certainly less than $\frac{1}{100}$ of a fringe and probably less than $\frac{1}{200}$.

The actual setting up of the apparatus was taken in hand about July 1920, and the site chosen was the compound of the Indian Association. One of the out-houses served to house the optical parts at the observing end, and a small hut was erected at the other end to receive the reflecting arrangement L_2R (fig. 1). The big telescope body with the object-glass was mounted on solid brick-work pillars erected for the purpose, and adjustments had to be provided for both vertical and horizontal movements. Some of these are shown in fig. 3 (Pl. VI.). A fine spectrometer slit was mounted at the eyepiece end of the telescope, and the thin plate-glass, P, was also mounted in the same tube. A microscope was used to observe the fringes. For the other end, another shorter telescope (4 inch objective) was similarly mounted on two pillars, and the eyepiece was in this case replaced by one of the front-silvered Michelson interferometer mirrors, so mounted as to allow of accurate adjustment of its plane. But the real difficulty lay in the fixing of the tubes. Galvanized-iron pipes of $1\frac{1}{2}$ in. internal bore were selected, and each piece was carefully straightened. Brick pillars were erected at intervals of about 10 ft., and their tops carefully aligned by means of a theodolite so that the deviations of the top line from the mean did not exceed $\frac{1}{10}$ of an inch for any individual pillar. This having been accomplished, the pipes were assembled and placed on top of the pillars, so that ultimately there was a pair of tubes quite straight from end to end and separated from each other by a constant distance throughout. There was no appreciable sag of the pipe between the pillars. This seems to have been avoided automatically by having such a considerable continuous length. This was finally tested by placing a small hole near one end and illuminating it by a strong beam of light. Observing at the other end, the whole of the aperture should be uniformly illuminated if there was no bend anywhere. Unfortunately this was very difficult to secure, for the slightest cutting-off of the light anywhere cast a tremendously large shadow at the great distance where it was being observed, and it was not at all easy to locate where the fault lay. The width of the diffraction fringes at the edge of the shadow, however, gave a rough and ready indication of the approximate position of the fault, and it was with the help of these that finally the major part of the aperture was freed from all obstacles. A parallel beam of light now sent down any one of the tubes passed unobstructed and filled almost the whole aperture at the other end.

The ends of the tubes were closed by windows of about $\frac{3}{4}$ in. diameter covered by thick interferometer plates secured between leather washers very much after the manner employed by Zeeman[*], and the current of air was led into the pipe by two side tubes inclined at about 60° to the axis of the pipe. The end pieces for carrying the windows and these inlet tubes were cast in brass, and can be seen in fig. 6 (Pl. VII.)

This method of leading the current of air into and out of the tubes is calculated to cause the least disturbance in the path of the light.

The manner of connecting the two tubes with each other at one end and with the arrangement of cocks to facilitate the reversing the direction of flow of air at the other, is shown in figs. 5 and 6 (Pl. VII.). This connexion is by means of lead pipes, and the reversing arrangement consists of four cocks connected by means of a handle, so that at any time two alternate cocks are open and the other two simultaneously closed. The central vertical pipe in the photograph leads to the blower, which was used rather as an exhauster, so that the air of the atmosphere entered one of the open cocks of the reversing arrangement, passed through one pipe to the other end, and returned through the other pipe and thence into the blower. This method was followed in order to avoid the temperature changes which would have certainly occurred within the tubes if the compressed air from the blower had been led into them. The temperature of the whole of the air in the tubes was thus kept equal to that of the external atmosphere.

With all these arrangements complete in January 1921, the two telescopes were carefully adjusted so that a fine slit sent two parallel beams down each tube, and the reflecting mirror at the other end sent them back still strictly parallel. It is evident that the slightest want of adjustment in the direction or the parallelism of the beams was enough to stop all light from passing through the tubes, and even the smallest angle between the two surfaces of each plate closing the ends of the tubes was inadmissible. But when these adjustments were carefully carried out, the fringes obtained were excellent and surprisingly steady, though the light

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[*] *Loc. cit.*

itself "boiled" very badly, except in the cool mornings. The heat of the sun during the day caused variations in the temperature of the air inside the pipes, and the convection currents deflected the light in all sorts of ways. This was to some extent avoided by covering the entire length of the pipes by bamboo screens, but the most satisfactory results were obtained only in the mornings or an hour or two after the sun had gone down.

To test whether or not the paths traversed by the two interfering beams were identical, the method suggested by Michelson was employed. A plane-parallel plate of glass was inserted in front of one of the ends of the tube, and the effect of its rotation on the fringes was observed in the microscope. With the final adjustments no displacement of the fringes could be observed by this means, and there seemed to be no reason to doubt that the paths were really identical and not merely parallel.

The current of air was now turned on, but it was at once apparent that the air was not flowing at a constant rate, but was being driven through the tubes in puffs; and although nothing happened to the fringes which, whenever visible, appeared in the same position as when no current of air was flowing, yet the spots of light themselves "boiled" very badly indeed. An attempt was made to overcome this difficulty by inserting a reservoir of air to steady the motion, and, after some preliminary trials with a brickwork and cement reservoir which developed a leak and proved unsatisfactory, a large wooden box, 4 ft. × 4 ft. × 6 ft., covered over with galvanized-iron sheets was installed, and inserted in the line of flow of the air between the pipe-line and the blower (see fig. 3, Pl. VI.). This successfully checked the oscillations in the speed of the current of air, and the spot of light in the microscope containing the interference fringes could be steadily seen, even with the current of air running.

To measure the velocity of the air-current, a pair of Pitot tubes with water-manometer were inserted in the channel between the pipe-line and steadying reservoir.

3. *Results.*

When the arrangements including the steadying reservoir were complete in April 1921, it was found that the engine and blower were unequal to the task of drawing the air through the system at the originally estimated velocity of 50 metres per second, and that a speed of only about 20 metres per second could be attained. The hot weather which had then commenced also made the temperature conditions in the tubes very unfavourable for systematic work. Nevertheless, on two evenings when observations were made after a smart shower following an April nor'wester, the fringes were seen very steadily, and appeared to show a slight but unmistakeable shift on reversing the direction of the air-current. On the second occasion an attempt was made to estimate the magnitude of the shift by setting a cross wire on the fringes and comparing the shift observed on reversing the air-current with that produced by flexure of the microscope tube by a known small load. The shift was estimated to be about $\frac{1}{20}$ part of a fringe, which was of the right order of magnitude and in the direction indicated by theory. Subsequent attempts to confirm these observations and measurements under less favourable conditions proved unfruitful, as the fringes then showed a distinct *rotation* as a whole when the air-current was reversed. The rotation proved to be a very troublesome and disturbing factor, and before the cause of it could be ascertained and removed, the work had to be suspended, owing to the departure of one of us for Europe. While, therefore, the results so far obtained cannot be regarded as entirely conclusive, they hold out a distinct promise of success when the work is resumed under more favourable conditions, particularly if a more powerful blower with steady electric drive can be obtained and installed.

L. *Active Modifications of Hydrogen and Nitrogen produced by α Rays.* *By* F. H. Newman, *M.Sc.*, *Ph.D.*, *Head of the Physics Department*, *University College*, *Exeter* [*].

1. Introduction.

IT has been shown recently [†] that nitrogen and hydrogen are both absorbed in the electric discharge tube, in the presence of various elements, when an electric discharge passes through the gases. This effect is due, in part, to chemical action, and is greatest when the element under investigation is deposited on the cathode of the tube. The chemical action appears to be produced by the gases assuming active modifications when an electric discharge is

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[*] Communicated by the Author.

[†] Newman, Proc. Phys. Soc. xxxiii. part ii. (1921).

passed through them. Strutt[*] found that nitrogen drawn from a discharge tube had active properties, and concluded from his experiments that the modified form was atomic in composition. Wendt[†] has shown that a modified form of hydrogen, probably consisting of H_3, is produced when an electric discharge passes through hydrogen at low pressures. In both cases the active form is not due to the ions produced.

The radiations from radioactive bodies, and especially the α rays, produce marked chemical effects in many substances. In general, the chemical actions produced resemble those due to the silent electric discharge. In some cases complex molecules are dissociated, in others more complex molecules are built up. Thus ozone is produced from oxygen. Carbon dioxide is transformed into carbon, carbon monoxide, and oxygen. Carbon monoxide is decomposed with the appearance of solid carbon and oxygen. Ammonia is changed into nitrogen and hydrogen, and in all cases the chemical action is proportional to the amount of radioactive body present, showing that the transformation of each atom of the radioactive body produces a definite chemical effect.

It would be expected that the effect of the rays from any radioactive substance, more particularly the α rays, would be similar to the electric discharge at low pressure. It should be possible to produce the active forms of hydrogen and nitrogen by the α rays. The object of the present work was to "activate" these gases in this manner, and show by the formation of chemical compounds that the modified form of the gas is more active, chemically, than the ordinary gas.

2. *Description of Apparatus.*

The apparatus used is shown in fig. 1. The gas was prepared, and stored in a very pure condition in a reservoir from which it could enter D. The latter was a known volume (0·106 c.c.) enclosed between two taps. A was the experimental bulb containing the radioactive substance—an electrolytic deposit of polonium on the plate G. The support of the plate was sealed through a glass stopper. The polonium could thus be removed while the bulb A was being cleaned after each experiment. The element used was introduced by the side tube B. The whole of the apparatus was evacuated by a Toepler pump. F and E were

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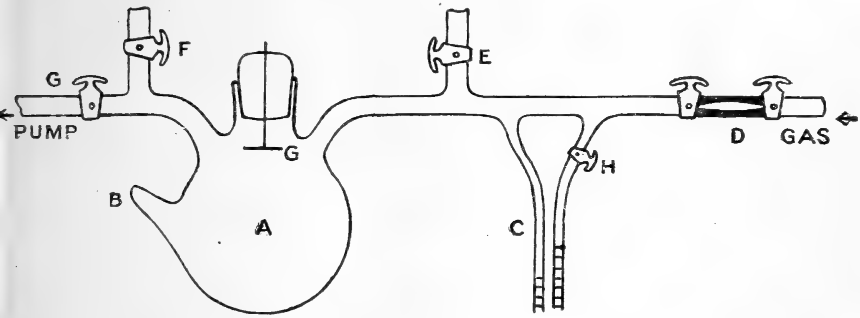
[*] Proc. Roy. Soc. lxxxv. (1911).

[†] Nat. Acad. Sci. Proc. v. (1919).

entrance and exit tubes respectively for moist air, used in the detection of chemical compounds produced. As a rule, the active gases will not react with any element unless the surface of the latter is clean and free from occluded gas. In all experiments a thin film of the substance being tested was deposited over the surface of A by distillation in vacuum. The volume of A was about 50 c.c.

Fig. 1.



3. *Experiments with Nitrogen.*

The nitrogen used was prepared by warming a solution of sodium nitrite and ammonium chloride. The gas was then passed over sodium-potassium alloy, calcium chloride, and phosphorus pentoxide to the reservoir. The whole of the apparatus was thoroughly washed out with nitrogen. The gas was then pumped out, and the element at the bottom of A heated to produce the pure deposit on the interior of A, care being taken that there was no film formed on G. Again the apparatus was evacuated, and the gases liberated by the melting of the element were removed. The tap H being closed, the oil manometer C was calibrated by admitting known volumes of gas from D, the pressure before and after the gas was admitted being noted. The α rays then acted on the gas in A, producing active nitrogen which combined chemically with the element present. As a result the gas gradually disappeared, this absorption being shown by a gradual decrease in the pressure indicated by C. From the initial and final readings of C the amount of gas absorbed could be calculated. This was repeated, using different pressures of gas. The polonium was never more than 6 cm. away from any part of A, and the range of the α rays was always greater than this distance, at the pressures used. The latter were measured by a mercury gauge, not shown in the diagram.

The substances selected were those which are fairly volatile in vacuum. The temperature of the experimental bulb A was maintained at −40° C. by immersion in a freezing mixture. Table I. shows that the rate of absorption increased as the pressure of the gas increased. The chemical effect due to the α rays, which is not necessarily equivalent to the ionization and probably exceeds the latter, appears to be a function only of the velocity of the α rays and of the number of collisions with the gas molecules. As the pressure decreases, the number of molecules present decreases, and as a result the amount of chemical action decreases. After absorption had occurred no gas was re-liberated when the bulb A was heated to 100° C. The chemical compounds produced must be fairly stable. The disappearance of the gas continued for many hours, but the rate of the absorption decreased with time, and finally ceased altogether. If the substance was re-heated, so that a fresh surface was prepared, the absorption re-commenced. The chemical compound produced at the surface of the substance protects the solid from further action, and accounts for this fatigue effect; unless the surface under examination was very clean there was no absorption at all. When about 3 c.c. of the gas had been absorbed by the sodium-potassium alloy, moist air was drawn through the bulb A from F to E, and was then passed through Nessler's solution. The presence of ammonia in the stream of air showed that the nitrides of sodium and potassium had been produced. A null experiment indicated that this ammonia was not present as an impurity in the air. The product obtained with magnesium was boiled with caustic potash, and the formation of a nitride was shown by the

TABLE I.

Substance.	Volume of nitrogen (at 760 mm. pressure) absorbed in 30 mins.		
	Pressure 3 mm. Hg.	Pressure 96 mm. Hg.	Pressure 304 mm. Hg.
Sodium	0·04 c.c.	0·07 c.c.	0·24 c.c.
Potassium	0·05	0·07	0·27
Sodium-Potassium alloy	0·09	0·11	0·36
Sulphur	0·11	0·14	0·48
Phosphorus	0·12	0·16	0·51
Iodine	0·09	0·11	0·46
Arsenic	0·01	0·08	0·21
Magnesium	0·03	0·06	0·19
Mercury	0·04	0·08	0·21

ammonia test. Negative results were obtained with sulphur, iodine, and phosphorus when tested for nitrides. The absorption cannot be due to occlusion, otherwise the gas would have been re-liberated on heating. The effect must be due, in some cases at any rate, to chemical action.

4. *Experiments with Hydrogen.*

The gas was prepared by the electrolysis of barium hydrate. After passing over sodium-potassium alloy to remove any oxygen, and then over phosphorus pentoxide, it was stored in a reservoir. Experiments were conducted in the same manner as those with nitrogen, but it was found that the gas was absorbed only by sulphur, phosphorus, and iodine. The results obtained are shown in Table II. The bulb was maintained at —40° C.

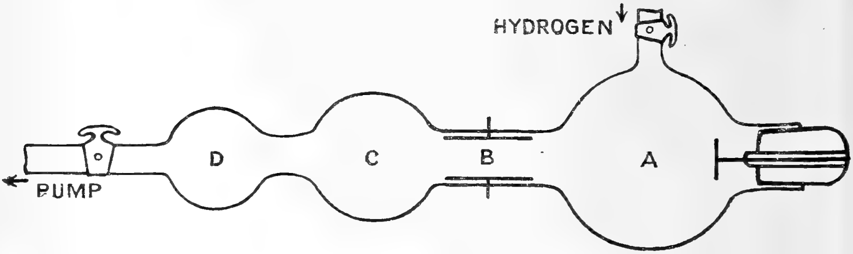
TABLE II.

Element.	Volume of hydrogen (at 760 mm. pressure) absorbed in 30 mins.		
	Pressure 5 mm. Hg.	Pressure 101 mm. Hg.	Pressure 299 mm. Hg.
Sulphur	0·09 c.c.	0·13 c.c.	0·46 c.c.
Phosphorus	0·10	0·16	0·49
Iodine	0·08	0·12	0·43

The rate of absorption decreased with time, and on heating the bulb to 100° C. most of the hydrogen which had been absorbed was re-liberated. This behaviour is different to that in the case of nitrogen. This indicates that with hydrogen the effect is either due to occlusion, or if it is due to chemical action, the resulting compounds must be unstable.

To show that the disappearance of the gas was due to chemical action, the apparatus shown in fig. 2 was utilized. Two strips of platinum foil, about 8 cm. long and fitting close to the interior of the glass tube, were introduced at B. The strips were connected to the terminals of a 600-volt water battery. Any ions present in the gas were removed as they passed through B. Sodium-potassium alloy was prepared in D, and, after the whole apparatus had been exhausted, the alloy was run into C. As a result, the alloy in C had a bright, clean surface. Hydrogen was then drawn through the apparatus, and was subject to the action of the α rays. When examined by a microscope, the surface at C was seen to be covered with a white crystalline substance, which afterwards changed into a blush-grey coloured film as more hydrogen was drawn through. The experiment was repeated without the polonium present, and in this case the surface of the alloy remained quite clear. The film produced is due to chemical action of the active hydrogen on the alloy. The white crystalline compound appears to be a mixture of the hydrides of sodium and potassium, while the bluish-grey coloured product afterwards formed is probably a solution of these hydrides in the alloy.

Fig. 2.



For the investigation of sulphur, a film of this element was deposited over the interior surface of C by distillation in vacuum. D contained some filter-paper soaked in lead-acetate solution, together with a little of the solution. After hydrogen, subject to the action of the α rays, had been drawn over the sulphur for about 30 minutes, the filter-paper in D became blackened. This indicated the presence of hydrogen sulphide in the stream of gas, and it had been produced by the action of the active hydrogen on the sulphur. A similar result has been found by Wendt and Landauer[*]. This chemical action is not due directly to the ions present in the gas, for they are all removed by the electrostatic field before coming into contact with the sulphur.

5. *Other Experiments.*

Some radium emanation of strength 57 mg., enclosed in a glass tube, was substituted for the polonium. The thickness of the glass—about 0·5 mm.—absorbed the α rays but transmitted the other rays. After several hours of test there was practically no absorption of hydrogen or nitrogen by any element: this indicates that the α rays are the effective ones in the chemical actions observed above.

Ultra-violet light was employed instead of the radioactive compound. A quartz-mercury lamp was used as the source of illumination, and the experimental bulb A was of

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[*] Amer. Chem. Soc. Journ. xlii. (1920).

quartz. There was, however, no sign of any activation in either gas. This negative result is explained either by the ultra-violet light not producing active gas, or by the quartz not being sufficiently transparent to those rays which produce the active modification.

The amount of gas absorbed was independent of the thickness of the element deposited on the glass surface: this indicates that the chemical action occurs at the surface.

The rate of absorption was increased by using a larger surface area of polonium, and was decreased when the temperature of the gas was raised. The activation of the gases thus appears to become greater as the temperature is lowered.

6. *Discussion of Results.*

Langmuir[*] found that hydrogen and nitrogen at low pressures disappeared in the presence of an incandescent tungsten filament, and he has utilized this fact in the elimination of the last traces of gas in valves, etc. The nitrogen forms a nitride with the tungsten. He accounted for the disappearance of the hydrogen by assuming that the molecules of the gas on impact with the hot filament are dissociated into atoms, and these atoms, at very low pressures, have a clear run to the walls of the vessel, and condense on them. This disappearance is marked at low temperatures. On heating the tube, Langmuir found that part of the gas was recovered. This re-liberated gas he supposes is due to the re-combination of the atoms driven off from the walls of the vessel by the heat.

At the pressures used in the present work, it is unlikely that the active gas consists of atoms. It is probably dissociated at first into atoms by the action of the α rays, and the atoms then unite with neutral molecules to form triatomic molecules. The existence of these triatomic forms of nitrogen and hydrogen has been shown by Wendt, in the papers previously quoted, by passing electric discharges through these gases at low pressures.

The function of the ions produced by the α rays does not appear to assist a chemical action between the gas and the element which does not otherwise take place, for the combination occurs after the ions have been removed. More probably the activity of the gas is due to an atomizing effect of the α rays on the gas, the active product being monatomic

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[*] Amer. Chem. Soc. Journ. xxxv. (1913); & xxxvii. (1915).

gas. Some of the atoms will be formed at the surface of the element, and will react chemically. Others will be produced in the interior of the gas, and will form triatomic molecules by collision with the neutral molecules. The primary action of the α rays appears to be the liberation of atoms of high activity. In addition, the rays produce δ rays by their motion through gases, and these δ rays may also be effective in producing the active modifications. The chemical actions occurring are probably determined by the heat necessary to effect the decomposition of the molecules, and not by the heat required for the final transformations and resulting products. That the α rays produce active modifications of hydrogen and nitrogen, which in turn are able to react chemically with certain elements, strengthens the view that the disappearance of these gases in an electric discharge tube, in the presence of various elements, is also due mainly to the formation of the active modifications of the gases by the electric discharge.

7. *Summary.*

1. α rays from polonium were allowed to act on nitrogen at different pressures in the presence of various elements. Some of the gas was absorbed.

2. The elements tested were sodium, potassium, sulphur, phosphorus, iodine, magnesium, arsenic, mercury, together with the alloy of sodium and potassium. Similar experiments with hydrogen gave absorption with sulphur, phosphorus, and iodine.

3. The absorption of the gas was shown to be due to chemical action resulting in the production of nitrides and hydrides.

4. The chemical activity of the gas is due to an active modification produced by the α rays. The active form, probably consisting of neutral atoms and triatomic molecules, is not due directly to the presence of ions.

5. The α rays are the only ones effective from radioactive bodies.

LI. *The Analysis of Microseismograms.*
By J. B. DALE, *M.A.* *

1. IN his monograph on Modern Seismology, Walker has called attention to the interesting records traced by seismographs when undisturbed by earthquakes.

Microseismic motion falls into two classes, of which one is due to the motion of wind and is wholly irregular, while the other prevails even in calm weather and at all times of the year, although it is more marked in winter than in summer. It is this latter type which is discussed in the present paper.

The general characteristics of the records of this seismic motion are smooth sinusoidal curves of fairly constant period, but with an amplitude which rises and falls at somewhat irregular intervals whose average length is about 1 minute. The period of the oscillations ranges from 4 to 8 seconds, the longer periods and larger average amplitudes occurring in the winter months.

Although the main features of the motion are obvious, their exact specification is by no means easy, and analysis discloses the simultaneous existence of oscillations of different periods. There also appear to be discontinuities in phase and period.

2. The method of analysis employed is that published by the writer a few years ago †, and the following summary will explain the notation. It is assumed that a function y of t can be expressed in the form

$$y=c_0+\Sigma c_n \sin(\theta_n t+\alpha_n), \quad . \quad . \quad . \quad . \quad (1)$$

when c_0, c_n, θ_n, α_n are constants to be determined from the observational data.

It is further assumed that the values of y are known for a sufficient number of equidistant values of t, the values corresponding to $t=0, 1, 2, \dots n$ being denoted by $y_0, y_1, y_2, \dots y_n$.

As a first step c_0 is eliminated by forming differences which are denoted by a, so that

$$a_r=y_{r+1}-y_r. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Next an operator E is defined by the relation

$$\mathrm{E}a_r=a_{r+1}+a_{r-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and in a similar manner E^2a_r, E^3a_r are derived.

The number of times the operation E is to be performed is equal to the number of independent periods. In practice

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* Communicated by the Author.

† "The Resolution of a Compound Periodic Function into Simple Periodic Functions," Monthly Notices, R. A. S., May 1914.

this number can be found only by trial. Supposing, for example, that three periodic terms are involved, then it must be possible to find constants p_1, p_2, p_3 such that the relation

$$E^3a_r + p_1E^2a_r + p_2Ea_r + p_3a_r = 0 \quad . \quad . \quad . \quad (4)$$

is identically satisfied for all values of r.

In any actual problem, on account of errors in the data it is impossible to satisfy this relation accurately; but if the residuals obtained on substituting successive values of a_r in the expression are always small and exhibit no systematic run, we may regard the assumption of three independent periodic terms as justified.

In the problem considered in the present paper it is found that the assumption of two periods satisfies this condition, and the relation to be satisfied is

$$E^2a + p_1Ea_r + p_2a_r = 0. \quad . \quad . \quad . \quad . \quad (4')$$

The values of p_1, p_2 are found by solving two of the equations.

With the values of the p's thus found, the equations

$$z^3 + p_1z^2 + p_2z + p_3 = 0 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or

$$z^2 + p_1z + p_2 \qquad = 0, \quad . \quad . \quad . \quad . \quad (5')$$

as the case may be, are formed and solved.

Considering (5), if the roots are z_1, z_2, z_3, then the three speeds θ_1, θ_2, θ_3 of the periodic terms are given by

$$\theta_1 = \cos^{-1}\tfrac{1}{2}z_1, \quad \theta_2 = \cos^{-1}\tfrac{1}{2}z_2, \quad \theta_3 = \cos^{-1}\tfrac{1}{2}z_3. \quad . \quad (6)$$

Finally, to obtain the amplitudes and arguments corresponding to θ_1, we form the series of quantities

$$P_r^1 = E^2a_r - (z_2 + z_3)Ea_r + z_2z_3a_r. \quad . \quad . \quad . \quad (7)$$

Then

$$c_1 \sin(\theta_1r + \alpha_1) = (P^1_{r-1} - P^1_r)S_1, \quad . \quad . \quad . \quad (8)$$

$$c_1 \cos(\theta_1r + \alpha_1) = (P^1_{r-1} + P^1_r)C_1, \quad . \quad . \quad (8')$$

where

$$C_1 = 1/2 \sin\theta_1(z_1 - z_2)(z_1 - z_3),$$

$$S_1 = 1/(2 - z_1)(z_1 - z_2)(z_1 - z_3) \quad . \quad . \quad . \quad (9)$$

In like manner the arguments and amplitudes of the other periodic terms are obtained.

3. The curve here submitted to analysis is part of that taken at Pulkowa, Sept. 18, 1910, and reproduced as Plate 7 A in Walker's book.

By means of tracing-paper ruled in millimetre squares, readings of the ordinates were taken at intervals of 1 mm.

The time-scale was such that 2·8 cm. corresponds to 1 minute; hence 1 mm. corresponds to 2·14 seconds. The ordinates are tabulated in units of 0·1 mm. The breadth of the trace being about 0·3 mm., it was not possible to read the values accurately in the neighbourhood of acute intersections of the curve with the ordinate lines, and so our readings may be 0·3 mm. or more in error.

4. The main steps in the determination of the periods of the oscillations prevailing during 1 minute are set out in Table I. It was found by trial that all the equations (4′) could be well satisfied by the assumption of only two periods.

TABLE I.

(1) t.	(2) y.	(3) a.	(4) Ea.	(5) E^2a.	(6) R.	(7) y'.	(8) R′.
0·0	31	+21				31	
1	52	− 7	+ 4			52	
2	45	−17	+25	−38	− 1	45	−4
3	28	+32	−42	+61	+ 4	29	−1
4	60	−25	+36	−48	+ 5	60	+1
5	35	+ 4	− 6	+ 9	− 1	33	+3
6	39	+19	−27	+27	−12	38	−3
7	58	−31	+33	−38	− 2	59	+2
8	27	+14	−11	+13	+ 6	29	−1
9	41	+20	−20	+24	+ 3	42	+1
1·0	61	−34	+35	−37	0	59	+1
1	27	+15	−17	+21	+ 1	28	−2
2	42	+17	−14	+10	0	43	+3
3	59	−29	+27	−20	+ 5	59	−1
4	30	+10	− 6	− 3	− 4	29	0
5	40	+23	−30	+41	+ 1	40	+1
6	63	−40	+47	−50	+ 7	65	+1
7	23	+24	−20	+21	+ 6	22	+1
8	47	+20	−26	+29	− 6	45	−4
9	67	−50	+49	−54	− 6	65	+1
2·0	17	+29	−28	+23	− 4	18	−3
1	46	+22	−26	+41	+ 9	47	+3
2	68	−55	+69	−88	+ 2	67	−1
3	13	+47	−62	+81	− 3	11	+1
4	60	− 7	+12	−27	− 8	59	+2
5	53	−35	+35	−43	− 8	54	−1
6	18	+42	−55	+73	− 1	20	−3
7	60	−20	+38	−59	+ 5	61	0
8	40	− 4	− 4			40	
9	36	+16				36	
3·0	52					52	

Column (1) gives the abscissæ, the common difference being 1 mm. or 2·14 seconds. Column (2) gives the corresponding ordinates y. Column (3) contains the differences (a), and columns (4) and (5) the values of Ea and E^2a.

Equations of the type $E^2a+p_1Ea+p_2a=0$ were formed and divided into two groups, the equations in each group being added to form a single equation.

From the two resultant equations the values of p_1 and p_2 were found to be

$$p_1=2{\cdot}4290, \qquad p_2=1{\cdot}4188. \quad . \quad . \quad . \quad (10)$$

Hence $$z_1=-{\cdot}9774, \qquad z_2=-1{\cdot}4516 \quad . \quad . \quad . \quad (11)$$

and $$\theta_1=119^\circ{\cdot}2, \qquad \theta_2=136^\circ{\cdot}5. \quad . \quad . \quad . \quad (12)$$

In order to test how far the assumption of the existence of only two independent periodic terms was justified, the values of $R=E^2a+p_1Ea+p_2a$ were calculated with the above values of p_1 and p_2 and are placed in column (6).

It is seen that with one or two exceptions the residuals are small and present no systematic run. Hence it is concluded that the deviations from zero are entirely due to errors in reading the values of y, and would be removed by appropriate corrections.

5. The determination of corrections is really an indeterminate problem, for the number of ordinates exceeds the number of equations. Expressed in terms of the y's, each equation $E^2a_r+p_1Ea_r+p_2a_r=0$ becomes

$$y_{r+3}+q_1y_{r+2}+q_2y_{r+1}-q_2y_r-q_1y_{r-1}-y_{r-2}=0, \quad (13)$$

where $q_1=p_1-1$ and $q_2=2+p_2-p_1$. . . . . . . (14)

The observed values, however, differ from the true values by small quantities v, and hence these deviations from the true values satisfy the equation

$$v_{r+3}+q_1v_{r+2}+q_2v_{r+1}-q_2v_r-q_1v_{r-1}-v_{r-2}=R_r. \quad (15)$$

To render the problem of finding appropriate values of the v's determinate, we add the condition that the sum of their squares must be a minimum.

Since the labour involved in obtaining an exact solution of the system of simultaneous equations arising from the expression of the problem in this form would be extremely great, it was decided to proceed by a method of successive approximation.

It is clear that any particular v will appear in six equations of the type (15), and these together with the minimum conditions will give a value for v. This method was tried, but was not found to lead to any more satisfactory results than those obtained by the simple method of obtaining six separate corrections to each v by solving equation (15) alone subject to the minimum condition.

Taking then (15) subject to

$$v^2_{r+3}+v^2_{r+2}+v^2_{r+1}+v^2_r+v^2_{r-1}+v^2_{r-2}$$

being a minimum, we obtain

$$\left.\begin{aligned} v_{r+3}=-v_{r-2}=\lambda, \qquad v_{r+2}=-v_{r-1}=q_1\lambda,\\ v_{r+1}=-v_r=q_2\lambda,\\ \text{where} \qquad \lambda=\mathrm{R}_r/2(1+q_1{}^2+q_2{}^2). \end{aligned}\right\} \quad \ldots \quad (16)$$

On repeating with the v's substituted for the corresponding y's the original series of operations, a new series of residuals was obtained whose average value was double the original R's. The values of y were therefore corrected by subtracting from them half the total values of the v's as given by the above formulæ. These corrected values of y are given in column (7) and the resulting residuals in column (8). It is seen that all large residuals have been removed, and this has been done without altering any y by more than two units, an amount well within the probable limits of error in reading the curve.

Seeing that the values of q_1 and q_2 are about unity, it is clear that an alteration of a y by a single unit may give rise to a unit residual; hence a complete removal of the residuals is difficult: but the fact that of the residuals only two are equal to 4, six are equal to 3, and the remainder are 1 or 0, shows that all the equations of conditions are now well satisfied.

6. We now proceed to determine the amplitudes and arguments of the component terms. With the corrected values y' we form fresh values of a and Ea (Table II.). This table also contains the values of $\mathrm{P}^1{}_r=\mathrm{E}a_r-z_2a_r$ (col. 4). Column (5) contains $\mathrm{S}_1\ (\mathrm{P}^1{}_{r-1}-\mathrm{P}^1{}_r)$ where $\mathrm{S}_1=1/(2-z_1)\times(z_1-z_2)=0{\cdot}71$, and column (6) $\mathrm{C}_1(\mathrm{P}^1{}_{r-1}+\mathrm{P}^1{}_r)$ where $\mathrm{C}_1=1/2\sin\theta_1(z_1-z_2)=1{\cdot}20$. In column (7) the corresponding arguments $\theta_1t+\alpha_1=\phi_1$ are tabulated, and in column (8) the amplitudes c_1. Column (10) contains the corresponding arguments ϕ_2 for the terms involving θ_2, and column (11) the values of c_2. These values are calculated with $\mathrm{S}_2=1/(2-z_2)(z_2-z_1)=-{\cdot}61$ and $c_2=1/2\sin\theta_2(z_2-z_1)=-1{\cdot}53$.

The last column gives the values of c_0, which are obtained by subtracting from y'_r the sum of the values of $\mathrm{S}_1(\mathrm{P}^1{}_{r-1}-\mathrm{P}^1{}_r)$ and $\mathrm{S}_2(\mathrm{P}^2{}_{r-1}-\mathrm{P}^2{}_r)$. The constancy of the values so obtained affords a check on the accuracy of the work and a further justification of the assumptions made.

TABLE II.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
t.	a.	Ea.	$P^1{}_r$.	$S_1(P^1{}_{r-1}-P'{}_r)$.	$C_1(P^1{}_{r-1}+P^1{}_r)$.	ϕ_1.	c_1.	$S_2(P^2{}_{r-1}-P^2{}_r)$.	ϕ_2	c_2.	c_0.
1	− 7	+ 5	− 3								
2	−16	+24	+ 1	− 2·9	− 2·4	230°	4	+ 6·1	146°	11	42
3	+31	−43	+ 2	− 0·7	+ 3·6	348	3	−12·8	301	15	43
4	−27	+36	− 3	+ 3·6	− 1·2	108	4	+14·0	72	15	42
5	+ 5	− 6	+ 1	− 2·9	− 2·4	230	4	− 6·7	206	15	43
6	+21	−25	+ 5	− 2·9	+ 7·2	338	9	− 2·4	345	10	43
7	−30	+34	−10	+10·7	− 6·0	119	12	+ 6·1	90	6	42
8	+13	−13	+ 6	−11·4	− 4·8	247	12	− 3·1	202	8	43
9	+17	−18	+ 7	− 0·7	+15·6	358	16	− 0·6	338	2	43
10	−31	+32	−13	+14·2	− 7·2	117	16	+ 1·8	130	2	43
1	+15	−15	+ 7	−14·2	− 7·2	243	16	− 1·2	201	3	43
2	+16	−15	+ 8	− 0·7	+18·0	358	18	+ 0·6	158	2	43
3	−20	+27	−16	+17·1	− 9·6	119	20	− 1·8	310	2	44
4	+11	− 5	+11	−17·1	− 6·0	251	18	+ 4·9	141	8	41
5	+25	−32	+ 4	+ 5·0	+18·0	16	18	− 8·5	290	9	43
6	−43	+48	−14	+12·8	−12·0	133	18	+ 8·5	70	9	44
7	+23	23	+10	−17·1	− 4·8	254	18	− 4·3	209	9	43
8	+20	−24	+ 5	+ 3·6	+18·0	11	19	− 2·4	345	9	44
9	−47	+49	−19	+17·1	−16·8	134	24	+ 4·9	58	6	43
20	+29	−27	+15	−24·2	− 4·8	259	25	− 1·2	191	6	43
1	+20	−27	+ 2	+ 9·3	+20·4	25	22	− 5·5	333	12	43
2	−56	+68	−13	+10·7	−13·2	141	17	+12·8	121	15	43
3	+48	−61	+ 9	−15·6	− 4·8	253	16	−16·4	275	16	43
4	− 5	+14	+ 7	+ 1·4	+19·2	4	19	+14·0	1	16	44
5	−34	+36	−13	+14·2	− 7·2	117	16	− 3·7	191	20	43
6	+41	−55	+ 5	−12·8	− 9·6	233	16	−11·0	329	21	44
7	−21	+37	+ 7	− 1·4	+14·4	354	15	+19·6	99	20	43
8	− 4	− 5	−11	+12·8	− 4·8	111	14	−15·8	232	20	43

7. The results here tabulated show numerous irregularities, but this is not surprising when we consider that the arguments and amplitudes ultimately depend upon the values of $P^1{}_r$ and $P^2{}_r$, all of which are less than 20 in absolute magnitude, and of which the majority are less than 10. Assuming the values of y' to be now correct within half a unit, and this is certainly not true in every case, there is a possible error of one unit in a and of two units in Ea. Hence $P^1{}_r$ which is equal to $Ea_r - z_2a_r$ may be over three units in error, and $P^2{}_r$ which is equal to $Ea - z_1a_r$ may be in error by nearly the same amount. Bearing this in mind, the consistency of the values obtained may be regarded as quite satisfactory.

An examination of the values of ϕ_1 shows a regular increase, in good agreement with the value for θ_1 obtained from the equation for the periods, namely 119°·2. A least square solution from the values obtained for ϕ_1 increases the value of θ_1 by a degree, making it 120°·2. This value indicates an oscillation whose period is three of the units of t or $6\frac{1}{2}$ seconds. But the values of c_1 show a rise from a value which is nearly zero to one of 25 followed by a fall. On plotting these values against the time, it is seen that they can be well represented by the expresion $22 \sin (6°t - 12°)$; and since the unit of time is 2·14 seconds, this indicates a complete fluctuation of amplitude in 2·14 minutes.

The phase when $t=0$ of the angle ϕ_1 may be taken without sensible error to be zero; hence the complete expression for the first periodic term becomes

$$22 \sin (6°t-12°) \sin 120°{\cdot}2t. \quad . \quad . \quad . \quad (17)$$

8. The values of ϕ_2 exhibit much greater irregularities than those of ϕ_1, particularly in the neighbourhood of $t=10$, where the amplitudes are nearly zero. If, however, we assume that there is a change of phase at this point of 180°, we can remove the most serious discrepancies. The mean of the first 9 values of ϕ_2 gives 323° as the argument at $t=6$, and the mean of the last 9 values gives 44° as the argument at $t=24$. Increasing 323° by 180° we obtain for the increment of ϕ_2 per unit of t, 134°·5, which is in good agreement with the value 136°·5 previously obtained.

Plotting the values of c_2 against t, taking those before $t=11$ to be negative on account of the change of phase by 180°, we find that the points are satisfactorily represented by $20 \sin (5°t-70°)$, and the complete expression for the second periodic term is

$$20 \sin (5°t-70°) \sin (134°{\cdot}5\, t+56°). \quad . \quad . \quad (18)$$

It is to be noted that no great degree of accuracy is claimed for the coefficients 6° and 5° of t in the factors $\sin (6°t-12°)$ and $\sin (5°t-70°)$, the data analysed being too restricted in extent for a closer determination, but they are probably correct to within 10 per cent.

9. An obvious interpretation of the results here obtained is that the microseismic motion was due to two groups of waves of periods of $6\frac{1}{2}$ and $5\frac{2}{3}$ seconds respectively. The group velocities were slightly different, but were of such an order that on the average each group attained a maximum within an interval of two minutes. Since the maximum amplitudes were nearly equal, the combination of the two

sets of waves gave rise to maxima at average intervals of one minute, and this feature is clearly shown on the records.

10. Another interpretation, however, is that the analysis employed has effected a separation of the observed movement into more than two simple harmonic components, for we may write

$$22 \sin (6^\circ t - 12^\circ) \sin 120^\circ{\cdot}2\, t + 20 \sin (5^\circ t - 70^\circ) \sin (134^\circ{\cdot}5\, t + 56^\circ)$$

in the form

$$11 \cos (114^\circ{\cdot}2\, t - 12^\circ) - 11 \cos (126^\circ{\cdot}2\, t - 12^\circ), + 10 \cos (129^\circ{\cdot}5\, t - 126^\circ) - 10 \cos (139^\circ{\cdot}5\, t - 14^\circ).$$

In view of the uncertainty attaching to the values found for the speeds, the terms

$$10 \cos (129^\circ{\cdot}5\, t - 126^\circ) \quad \text{and} \quad 11 \cos (126^\circ{\cdot}2\, t - 12^\circ)$$

are hardly distinguishable one from the other, and there is a possibility that the number of component harmonics is only three, with speeds about 114°, 127°, and 139°.

The smallness of the amplitudes makes a closer determination of the angles impossible. It is therefore desirable to see whether other portions of the seismogram confirm the result just obtained. The portion of the trace analysed formed part of the fifth line of Plate 7 A, and portions of the traces in the first, second, third, seventh, and eighth lines were measured and treated in the same manner.

As a rule, the equations of conditions were well satisfied by the assumption of the existence of two periodic terms, but in two cases somewhat smaller residuals were obtained by the assumption that three terms were involved.

The values of the speed angles thus found are here tabulated.

Line 1.	1st solution	129°·5,	114°·1	
	2nd solution	131°·6,	119°·8	
Line 2.	Assume two periods	134°·2,	115°·4	
	Assume three periods	134°·9,	122°·4,	82°·2.
Line 3.	Assume two periods	148°·7,	125°·5	
	Assume three periods	149°·5,	120°·2,	45°·5.
Line 5.	Assume two periods	134°·5,	120°·2	
	Since, however, the amplitudes vary, it is more correct to say that there are three periods whose speed values are	139°,	127°,	114°.
Line 7	....	129°·6,	112°·2	
Line 8	....	140°·9,	110°·0	

The results agree sufficiently well to establish the existence of at least two periodic terms, but the differences between the various solutions are so large that it is not easy to say whether three or even a greater number may not be involved.

The somewhat unsatisfactory nature of this conclusion is solely due to the circumstance that the measured ordinates may be in error by an amount of the order of one-tenth of the maximum amplitude of swing, and as analyses of artificially constructed functions show, small changes in the values of the ordinates make unexpectedly large alterations in the values of speed and other constants.

Until means are found for obtaining a higher degree of magnification of the movement, and, if possible, a diminution in the breadth of the trace, it will be difficult to obtain more definite results.

University of London,
King's College.
Aug. 1921.

LII. *An Interferometer Method of determining the Phase Difference resulting from Metallic Reflexion.* *By* H. P. Waran, *M.A., Government Scholar of the University of Madras* *.

[Plate VIII.]

WHILE investigating the possibility of a parallel plate interferometer, by floating one transparent liquid as water over another like mercury, the question arose as to the difficulties that would arise from the difference in the character of the reflexions from the two surfaces. In the parallel plate of glass both the surfaces are identical and the reflexions take place under identical conditions. But in the present case nearly total reflexion at the top water-air surface and simple reflexion at the bottom mercury surface are utilised to get multiple reflexions from the parallel plate of liquid. To see if this metallic reflexion at the bottom surface was producing any disturbing factor prejudicial to the success of this type of interferometer, a control experiment was devised with a glass Lummer plate which led to a very interesting observation.

The glass Lummer plate (made by Hilger) was mounted on a specially made ebonite mount, resembling very much the

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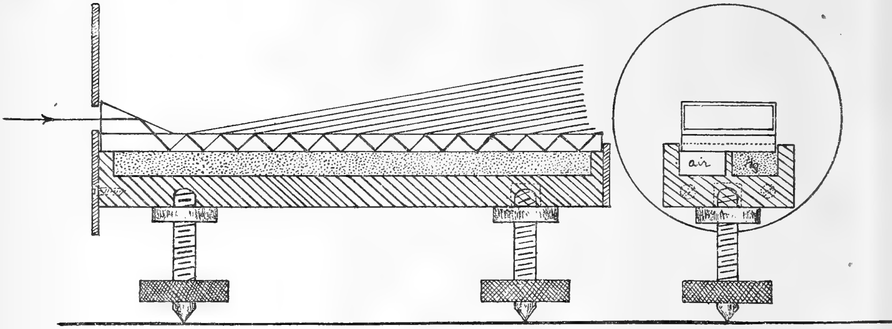
* Communicated by Prof. A. W. Porter, F.R.S.

usual brass mount, but provided with a trough arrangement as shown in fig. 1 in part section, by which clean mercury could be introduced below the plate and made to cover its bottom surface. This combination being of identical size with the usual mount of the parallel plate could be fitted on the Hilger interference spectroscope between the collimator and the constant deviation prism, as in fig. *a* (Pl. VIII.).

Fig. 1.



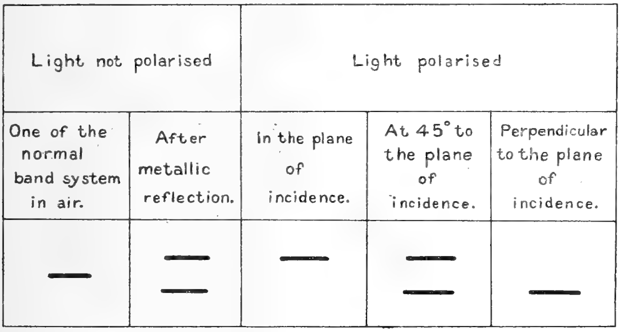
The slit was illuminated by a mercury vapour lamp, and the resulting interference pattern displayed an interesting change as shown by fig. *b* (Pl. VIII.). For the first appearance it was as if an extra system of bands had crept in between the normal system of bands. That it was not due to a simple reflected system was evident from the absence of constant spacing between the two sets of bands. An idea that it might be due to a thin layer of air between the glass and the mercury led to a repetition of the experiment by silvering the bottom surface of the plate chemically. The same type of band system observed made it conclusive that it was being brought about as an effect of the metallic reflexion at the bottom surface.

Considering the effect of such a metallic reflexion, we know from the optical properties of metals that the emergent light will be elliptically polarized. On this consideration, the extra system of bands could be explained away directly as due to a simple phase difference effect brought about by the metallic reflexion. In such a case the effect of polarizing the incident light ought to be to make one of these two systems of bands disappear as shown in fig. 2, according as the incident light is polarized in the plane of incidence or perpendicular to it. A Nicol polarizer introduced into the path of the incident light brings about this change as expected, confirming the validity of our explanation.

Considering the accuracy with which interferometer measurements could be conducted, it occurred to the writer that this method may be used for experimentally determining the phase difference resulting from metallic reflexion with greater accuracy, since it is free from the defects of other methods which suffer * from the unavoidable impurities of the polished metal surfaces exposed to air.

Before going into the theory of the method, a word may be said about the experimental arrangements adopted to secure the necessary photographs of the fringes for measurement.

Fig. 2.—Showing the types of changes resulting from metallic reflexion in polarized and unpolarized light.



The glass Lummer plate chemically silvered on the bottom surface was taken, and half the silvering along its length removed by gentle rubbing with dilute nitric acid, and the glass portion thus showing cleaned and dried carefully. It was then mounted in its usual stand on the Hilger interference spectroscope. Light from a mercury vapour lamp was focussed on the slit by a pair of collimating lenses, between which was interposed a 2 in. Nicol polarizer as illustrated in fig. *c* (Pl. VIII.). The polarizer was set to polarize the incident light in the plane of incidence, and thus cut off the other component set of bands resulting from the metallic reflexion and corresponding to the case of light polarized perpendicular to the plane of incidence. Under these circumstances, the collimated beam in passing through this half metal and half air plate was split into two halves, namely, the one that underwent metallic reflexion and the other that did not, and the fringes due to these two were obtained consecutively on the same plate, but with a natural

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* Drude's 'Theory of Optics,' p. 366.

displacement vertically between the two sets that represented the phase difference. The fringes due to the latter acted as the reference marks from which to measure the distance to the bands corresponding to the former, and a slight lateral shift given to the latter system of bands by rotating the wave-length drum a little served to identify the two in practice, as shown in fig. *d* (Pl. VIII.).

For mercury, which was the next metal studied, the arrangement had to be slightly modified, and the specially made ebonite trough described above and shown in fig. 1 and Pl. VIII. fig. *e*, had to be used. A modification had to be introduced in it in the form of a narrow partition to divide the mercury chamber into two longitudinal halves, so that, as with the silver, we might get half the plate covered with mercury, leaving the other half free as shown in part section fig. 1.

We may proceed now to consider the theory of the method and the process employed for the actual evaluation of the phase difference from a measurement of the displacement of the metal fringes from the normal system.

Let t = the thickness of the parallel plate and μ = the refractive index for the wave-length λ used, which may be calculated out from the given optical constants of the plate, using Cauchy's formulæ.

Then the path difference between two adjacent beams emerging out of the plate because of the multiple reflexions is given by the relation

$$2\mu t \cos r = n\lambda, \quad \ldots \ldots \quad (1)$$

where r is the angle of incidence for these rays within the plate.

If we count this as the path difference for the starting band of the Lummer system of fringes, we have a bright band at every position corresponding to an increase in the path difference by λ. Thus for the pth band we have

$$2\mu t \cos (r - \delta r_p) = (n+p)\lambda. \quad \ldots \ldots \quad (2)$$

Subtracting (1) from (2), we have, since δr_p is small,

$$2\mu t \sin r \, \delta r_p = p\lambda. \quad \ldots \ldots \quad (3)$$

Further, we have the relations

$$\sin i = \mu \sin r,$$

and

$$\sin i_p = \mu \sin r_p,$$

$$\therefore \quad \sin i - \sin i_p = \mu (\sin r - \sin r_p)$$

$$= \mu . 2 . \cos \frac{r + r_p}{2} \sin \frac{r - r_p}{2} .$$

But

$$\frac{r+r_p}{2} = r \text{ approx.} \quad \text{and} \quad \sin\frac{r-r_p}{2} = \sin\frac{\delta r_r}{2} = \frac{\delta r_p}{2}.$$

Therefore $\qquad \sin i - \sin i_p = \mu \cos r \, \delta r_p. \qquad (4)$

But from (3)

$$\delta r_p = \frac{p\lambda}{2\mu t \sin r}$$

substituting in (4) for δr_p we get

$$\sin i - \sin i_p = \frac{\mu \cos r p\lambda}{2\mu t \sin r}$$

$$= \frac{p\lambda}{2t \tan r}.$$

Expanding

$$2 \cos\frac{i+i_p}{2} \sin\frac{i-i_p}{2} = \frac{p\lambda}{2t \tan r} = \mathrm{K}p,$$

where $\qquad \mathrm{K} = \dfrac{\lambda}{2t \tan r}.$

Let $\qquad i - i_p = \theta_p, \quad$ so that $\quad i_p = i - \theta_p,$

and

$$\frac{i+i_p}{2} = i - \frac{\theta_p}{2},$$

and

$$\sin\frac{i-i_p}{2} = \sin\frac{\theta_p}{2} = \frac{\theta_p}{2}.$$

∴ We get

$$\cos\left(i - \frac{\theta_p}{2}\right) = \frac{\mathrm{K}p}{\theta_p}. \qquad (5)$$

Now θ_p can be found by observation of the distance of the *p*th band from the zero band and dividing it by the focal length of the camera lens. Substituting in equation (5) gives us the value of i, since k is readily evaluated from the known constants. By taking every value of p from 1 upwards, the corresponding value of i is deduced and the mean value of i found out. Values of i for the successive bands can then be found out by calculation from the relation

$$\sin i_p = \sin i - \mathrm{K}p. \qquad (6)$$

After this preliminary consideration of the elementary theory applicable to the present case, we proceed as follows to apply it to the case of metallic reflexion. When simple multiple reflexion takes place in a parallel plate of glass bounded by air, we have the simple relation

$$2\mu t \cos r = n\lambda.$$

But, for the case of light reflected from one of the surfaces covered by metal and polarized in the plane of incidence, this becomes

$$2\mu t \cos(r+\delta r) + \frac{\theta}{2\pi}\lambda = n\lambda \quad . \quad . \quad . \quad . \quad (7)$$

when we account for the displaced band as being due to a change of phase on metallic reflexion. When the band shifts to its new position as a result of the phase difference, the change in the angle of incidence corresponds to the term δr and the phase difference of θ is taken into consideration by the term $\frac{\theta}{2\pi}\lambda$.

Expanding (7),

$$2\mu t \cos r \cos \delta r - 2\mu t \sin r \sin \delta r + \frac{\theta}{2\pi}\lambda = n\lambda,$$

i. e. $$2\mu t \cos r - 2\mu t \sin r\, \delta r + \frac{\theta}{2\pi}\lambda = n\lambda,$$

i. e. $$n\lambda - 2\mu t \sin r\, \delta r + \frac{\theta}{2\pi}\lambda = n\lambda,$$

i. e. $$2\mu t \sin r\, \delta r = \frac{\theta}{2\pi}\lambda,$$

and therefore

$$\theta = \frac{2\pi}{\lambda} 2\mu t \sin r\, \delta r. \quad . \quad . \quad . \quad (8)$$

But $$\sin i = \mu \sin r.$$

Differentiating $$\cos i\, \delta i = \mu \cos r\, \delta r.$$

Therefore $$\delta r = \frac{\cos i\, \delta i}{\mu \cos r}.$$

Substituting for δr in (8)

$$\theta = \frac{2\pi}{\lambda}(2\mu t \sin r)\frac{\cos i\, \delta i}{\mu \cos r}$$

$$= \frac{4\pi}{\lambda} t \tan r \cos i\, \delta i$$

$$= \mathrm{K}' \cos i\, \delta i, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $$\mathrm{K}' = \frac{4\pi}{\lambda} t \tan r.$$

In practice, with the constant K′ evaluated from the known constants of the plate, to evaluate θ the phase difference, the normal (glass-air) system of bands is measured out, and getting by subtraction the distance of each from 0 and dividing by the focal length of the camera, the values of θ_p and therefrom the mean i, i_p, and $\cos i_p$ for each value of p are evaluated. In each case δi_p is given by the measured displacement on the plate of the metallic fringe from the normal system divided by the focal length of the camera lens. The mean of the values of $\cos i_p \, \delta i_p$ for each of the values of p is the value for $\cos i \, \delta i$ employed in the final substitution in (9) to give the value of the phase difference.

In practice, the method works out quite satisfactorily, and the preliminary study in the case of silver and mercury has yielded quite concordant results. Because of freedom from surface impurities in the present method, and considering that the effect of surface impurities is to lower the values, the slightly higher values obtained by this method are easily explained. This view has also in corroboration the fact of the observed difference in the case of mercury being much smaller than with silver, which is more liable to surface contamination than mercury. Further, the method has also the advantage of being applicable to all the other metals which can be coated on to the Interferometer plate by cathodic deposition or otherwise. A detailed evaluation of this phase difference for all the metals is in progress.

In conclusion, I beg to express my indebtedness to Prof. R. Ll. Jones, M.A., Professor of Physics, Presidency College, Madras, for his kind and sympathetic help during the progress this investigation at Madras under his direction.

University College,
London.

LIII. *Stopping Power and Atomic Number.*

By J. L. Glasson, *M.A.*, *D.Sc.*[*]

1. It has recently been established that certain properties of the atom are more simply and accurately expressed in terms of atomic number than in terms of atomic weight. The following is an attempt to find out if this is also true of the atomic property known as stopping power for α rays.

According to the work of Sir William Bragg, it was shown that the stopping power of an atom is proportional to the square root of the weight of the atom. Professor Bragg's own figures which form the basis of the work are given in

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[*] Communicated by Prof. Sir E. Rutherford, F.R.S.

columns III. and IV. of Table I. The value for argon is that obtained by Adams (Phys. Rev. vol. xxiv. p. 108, 1907). The constancy of the figures in column IV. is a measure of the range and of the success of the rule.

TABLE I.

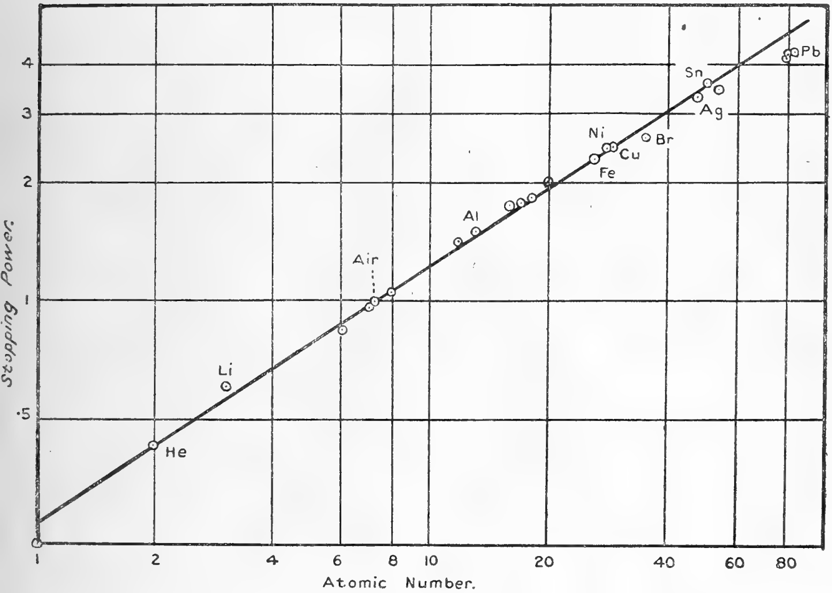
I.	II.	III.	IV.	V.	VI.	VII.
Symbol.	At. Wt.	Stopping Power.	$\frac{\sigma}{\sqrt{w}}$.	At. No.	$N^{\frac{2}{3}}$.	$\frac{\sigma}{N^{\frac{2}{3}}}$.
H	1	·24	240	1	1·00	240
He	4	·43	214	2	1·59	269
C	12	·85	246	6	3·30	256
N	14	·94	252	7	3·66	256
Air	**14·4**	**1·00**	**264**	**7·2**	**3·71**	**269**
O	16	1·05	262	8	4·00	262
Al	27	1·49	288	13	5·52	270
S............	32	1·76	312	16	6·36	275
Cl	35·5	1·78	299	17	6·60	270
A	40	1·83	290	18	6·87	267
Fe	56	2·29	307	26	8·77	260
Ni	59	2·44	319	28	9·21	262
Cu	64	2·46	309	29	9·44	262
Br	80	2·60	291	35	10·7	242
Ag	108	3·28	315	47	13·0	253
Sn	119	3·56	326	50	13·6	260
I	127	3·44	307	53	14·1	244
Pt	195	4·14	297	78	18·2	227
Au	197	4·22	301	79	18·4	228
Pb	207	4·27	298	82	18·9	226

2. In fig. 1 the logarithms of the atomic stopping power are plotted against the logarithms of the atomic number. The observed values lie nearly on a straight line whose slope is almost exactly two-thirds. In fig. 1 the line is drawn so as to pass through the air or standard point and have the slope two-thirds. It will be seen that it fits the observations very well. The relation between σ and N is of the form $\sigma=kN^{\frac{2}{3}}$, where $k=\cdot262$ and is the atomic stopping power of hydrogen. We may say therefore that "*The stopping power of an atom is proportional to its atomic number raised to the power two-thirds.*"

3. It is perhaps desirable to inquire how well this rule fits the observed values and to compare its success with

Bragg's rule. The limitations in one respect are the same for both. They do not apply when large velocity variations are permitted in the α rays employed. Nevertheless Bragg's rule is extremely useful over a considerable range of speeds, and there is no reason to believe that the new rule should be less applicable over the same range. The degree of numerical agreement is shown by the figures in columns V., VI., and VII. of the Table. The constancy of the numbers in column VII. is the measure of the success of the rule. The average deviation from the mean is 5 per cent. for column VII. as against 8·3 per cent. for column IV. The maximum deviation is 11 per cent. as against 25 per cent. for the square root rule. The case of the helium-hydrogen ratio is interesting. According to the square root law, remembering that hydrogen is diatomic, the stopping powers of the two gases should be equal. All the observations prior to 1914 had made the ranges of α particles nearly the same for the two gases, that in helium being slightly less than that in hydrogen. In 1914 Taylor found (Phil. Mag. vol. xxvi. p. 402, 1914) that if special precautions were taken to purify the helium, then the range was actually 5 per cent. greater in helium

Fig. 1.



than in hydrogen. This is a remarkable result when we consider that the density of helium is twice that of hydrogen. Nevertheless it is successfully predicted by the atomic number rule, but not by the atomic weight rule.

4. There is a recent paper by von Traubenberg (*Zeitschrift für Physik*, vol. ii. p. 268, 1920) dealing with the range of α particles, in the first part of which he describes a new method of determining the range of α particles in solids, which is apparently simple and accurate. But the values of the stopping power deduced from these ranges depend on the value given to the range of the α particle in air, and no uniform value has been employed by different experimenters. Until therefore this new method has established itself in the confidence of experimenters in this field and, more important perhaps, until the meaning of the word range is more clearly defined by them, I have thought it best not to endeavour to incorporate von Traubenberg's results into Bragg's table. But a study of them leads to three conclusions :—

(1) The two-thirds power rule fits von Traubenberg's results as accurately as it does Bragg's.
(2) The stopping powers of platinum, gold, and lead are distinctly greater than those determined by Bragg. Thus the slight deviations which these three elements show in fig. 1 are reduced to about half their present amount.
(3) The new elements lithium, magnesium, and calcium are made available. I have inserted these in fig. 1 and they fit well.

In the second part of his paper and in another paper (*Phys. Zeit.* p. 588, 1920) von Traubenberg examines the agreement of his results with Bragg's rule and, finding the well-known discrepancies in the region of low atomic weights, tests certain new rules which give, he claims, better agreement than Bragg's. The first two of these express the stopping power as a complicated function of both atomic weight and atomic number. One is that σ is proportional to $AN^{\frac{1}{2}}$. The other is that σ is proportional to $A^{\frac{1}{6}} N^{\frac{1}{3}}$. These fit slightly better than Bragg's in the region of high atomic weights, but distinctly worse in the region of low atomic weights as von Traubenberg himself shows. Neither of them predicts the hydrogen-helium ratio to which attention has been drawn. A third rule, that the stopping power is proportional to the square root of the atomic number, fails to express the results either for high or for low atomic weights.

It is important to notice that for the test of a *power* law the first nine elements are as important as the other seventy-three taken together. In the upper part of the table the rate of variation of stopping power and of atomic number is not nearly so rapid, and many rules could be devised which would fit the results over a limited range of the periodic table. The logarithmic plotting which is used in the figure brings out this fact, whereas the method of direct plotting which von Traubenberg uses disguises it.

It seems evident, therefore, that while von Traubenberg's experimental results are a valuable addition to our knowledge, his rules fail either in simplicity or in generality or in both.

5. In view of the complexity of the phenomena associated with the passage of α rays through matter, it is rather surprising that a simple relation can be found between stopping power and atomic number. The index number suggests that the stopping power of an atom is related to the number of electrons in the atom in much the same way as the cross section of a sphere is related to its volume. A theory of the passage of α rays through matter has been worked out by Bohr (Phil. Mag. vol. xxx. p. 581. 1915), and it has been shown by him to express the results for light atoms. The data necessary for applying it to heavy atoms are unfortunately not available. The two-thirds power rule is therefore propounded as a simple working rule until such time as a general theory of the phenomena is available.

Cavendish Laboratory,
Cambridge,
October 11, 1921.

LIV. *The Dielectric Constants of some of the Esters at Low Temperatures.* By L. C. Jackson, *M.Sc.*[*]

THE dielectric constants of the members of homologous series of organic compounds, when measured at ordinary temperatures, are generally found to change from member to member in a manner that can be correlated with the structure of the compounds. This is exemplified in the case of the two series of esters (formates and acetates) for which the values of the dielectric constants as determined by Drude[†] by his well-known method, using high-frequency oscillations, are given below. It will be seen that the values

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[*] Communicated by the Author.

[†] *Zeit. Phys. Chem.* xxiii. p. 267 (1897).

change fairly regularly from member to member of each series, and that the values for the corresponding members of the two series are distinctly different.

Methyl formate	8·87 (19°)	Methyl acetate	7·03 (20°)
Ethyl formate	8·27 (19°)	Ethyl acetate	5·85 (20°)
n-Propyl formate	7·72 (19°)	n-Propyl acetate	5·65 (19°)
n-Butyl formate	—	n-Butyl acetate	5·00 (19°)

The figures in brackets are the temperatures at which the determinations were made.

The object of the present work was to determine the values of the dielectric constants of the above series of esters at the low temperatures obtainable with liquid air so as to find the actual values of the dielectric constants and compare them with those obtaining at ordinary room temperatures, and to find whether the relations holding at ordinary temperatures between the various members of the series and between corresponding members of the series of formates and acetates hold also at the lower temperatures.

The results obtained, for which great accuracy is not claimed and which are intended as preliminary values, show that apparently the acid radicle contributes but little, as compared with the rest of the molecule, to the value of the dielectric constant at the temperature of liquid air, since the constants for the corresponding formates and acetates are found to be approximately equal. The values for the various members of either series do not apparently exhibit the same relationships to each other as hold at ordinary temperatures.

Method of Experiment.

The principle underlying the method used in the present work may be stated briefly as follows:—An electric circuit containing a capacity C and an inductance L will oscillate with a frequency determined by the relation

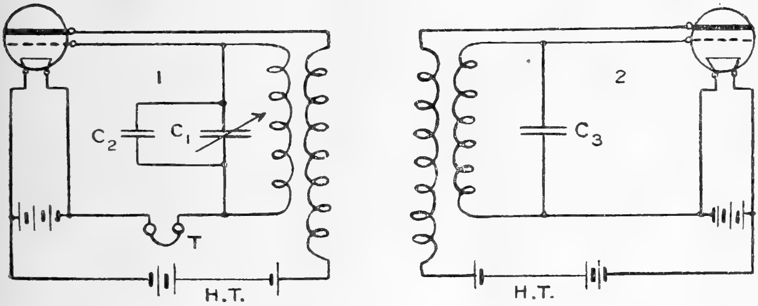
$$T=2\pi\sqrt{LC},$$

where T is the time of oscillation.

If, now, a second condenser is connected in parallel with the first one, and the latter is so reduced that the frequency of oscillation of the circuit is the same as in the absence of the second condenser, first when the latter has air (or, more correctly, a vacuum) as its dielectric, and secondly some other substance, the ratio of the amounts by which the first condenser had to be reduced in the two cases will give the dielectric constant of the substance under test for the particular conditions of temperature and frequency of oscillation obtaining at the time of the experiment.

The actual arrangement by which the above-described method was applied to the investigation of the dielectric constants of the esters is shown diagramatically in fig. 1. It consists of two simple "valve" circuits placed side by side, so that, as in the heterodyne method of reception, a beat note is heard in the telephone placed in one of the circuits. In parallel with the variable condenser C_1 is placed the experimental condenser C_2, the change of the capacity of which with change of dielectric is to be determined. The circuit 2 remains untouched throughout the experiment, and serves as a means whereby the frequency of oscillation of circuit 1 can be brought to some standard value whenever required. The method actually adopted for this purpose was to adjust C_1 so that the beat note in the telephone always just fell to zero. The accuracy with which the scale of the variable condenser could be read determined the accuracy with which it was necessary to adjust the beat note to the standard value, it being found that the method of adjusting to zero gave all the accuracy of setting required, so that the more elaborate and accurate method of comparing the beat note with a standard fork was not used.

Fig. 1.



The experimental condenser was a brass cylindrical one, consisting of four coaxial tubes connected together alternately and fastened at one end into a fibre separator. The diameter and length of the outer tube were 2·06 cms. and 12·36 cms. respectively, this size being such that the condenser would just slip into an ordinary boiling-tube.

The whole of the two circuits, with the exception of C_2 and the telephones T, was enclosed in an earthed tin-plate case to prevent any change in the frequency of oscillation of the two circuits being caused by external disturbances or the movements of the observer. This precaution was quite necessary for accurate work on account of the well-known delicacy of the arrangement. It was also necessary to keep the whole apparatus dry throughout.

The procedure of the experiments was as follows:—The variable condenser C_1 was adjusted until the beat note fell to zero when the experimental condenser was removed from the outer end of the leads. The condenser C_2 with air as dielectric was then attached and the process repeated. The air was then replaced by the substance to be tested, and the whole, which was contained in an ordinary boiling-tube, was placed in a bath of liquid air. The test substance solidified (the substances used in the work being all liquid at room temperatures), and was allowed to remain in the liquid air until a constant state was obtained, and the condenser C_1 adjusted as before.

The shifts of the condenser C_1 gave first the capacity of C_2 with air as the dielectric, and secondly with the test substance, the ratio of the two shifts (after being suitably corrected) being the value of the dielectric constant of the test substance at the temperature of the liquid-air bath and for the particular frequency of the oscillations used.

The temperatures were measured throughout by means of a platinum resistance thermometer, and the frequency of the oscillations with the aid of a wave-meter.

Care was taken to make the measurements of the capacity of C_2 with air and with the test substance as dielectric under as nearly as possible identical conditions (except as to temperature—see below), and the effect of the leads was eliminated by keeping them permanently attached to C_1 so that the difference of any two readings on C_1 did not contain any contribution from them.

The scale of the variable condenser having been previously calibrated, a correction may be applied to the observed values for the known unevenness of the scale. The fact that the capacity of C_2 with air as dielectric was measured at ordinary temperatures and with the test substance at the temperature of the liquid-air bath, necessitated a correction for the temperature change of the dimensions of the condenser.

Quite recently a number of methods for the application of "valve" circuits to the measurement of capacities have been described by several investigators: arrangements similar to the above have been proposed by J. Scott Taggart ('Electrician,' lxxxii. pp. 466–467, Apr. 18, 1919) and J. Herweg

(*Deutsch. Phys. Ges. Ver.* xxi. pp. 572–577, Sept. 30, 1919), and more complicated methods involving the use of more than two valve circuits have been described by Pungs and Preuner (*Phys. Zeit.* xx. pp. 543–545, Dec. 1, 1919) and Falckenberg (*Ann. der Phys.* lxi. 2, pp. 167–172, Jan. 15, 1920). The latter worker has applied his method to the determination of the dependence on pressure of the dielectric constants of water, ethyl alcohol, methyl alcohol, and acetone.

Purification of the Materials.

The substances used in the investigation were methyl, ethyl, n-propyl, n-butyl formates and the corresponding acetates. The esters were obtained from the firm of Poulenc Frères of Paris, and before use were fractionated, washed, very carefully dried, and re-distilled. It was found, however, that after the most elaborate precautions had been taken to eliminate water, acids, or other possible impurities, the methyl, ethyl, and, to a less extent, n-propyl esters still possessed a conductivity, while liquid at ordinary temperatures, which, though very small, was sufficient to so reduce the intensity of the sound in the telephones as to make the method inapplicable, quite apart from any change in the value of the effective dielectric constant due to the finite conductivity of the dielectric. (Had it been possible to obtain readings of C_1, the true dielectric constant could have been calculated in terms of the known resistance of the dielectric and the constants of the circuit: *cf.* R. T. Lattey, Phil. Mag., June 1921. Possibly some arrangement by which the sound in the telephones could be considerably amplified would enable this to be done.)

In the case of the butyl esters it was found that a much less rigorous method of purification than had failed with the other esters would suffice to reduce the conductivity, even when the substances were liquid to a value small enough to make the method applicable.

The facts that the conductivity of the esters remained after very rigorous purification, and that this residual small conductivity decreased from member to member as one proceeded up the series, would seem to show that this conductivity was a property of the esters themselves.

The conductivities of the esters when solid at liquid-air temperatures were so small as to make the present method quite applicable. In general, the method provides a very simple and direct means of measuring the dielectric constants of substances of sufficiently small natural conductivity.

Experimental Results.

The results obtained for the dielectric constants of esters at the temperature of liquid air are exhibited in tabular form below. The values have been corrected for the inequalities of the condenser scale and for the temperature change of the dimensions of the experimental condenser.

TABLE I.

Substance.	Temperature T.		Dielectric Constant at temperature T.		Dielectric Constant at ordinary temperature.
	Obs.	Mean.	Obs.	Mean.	
Methyl formate.	76°·8 A	78°·65 A	2·54	2·56	8·87
	78·°0 A		2·57		
	82°·8 A		2·52		
	77°·0 A		2·615		
Ethyl formate.	83°·2 A	81°·3 A	2·38	2·40	8·27
	82°·0 A		2·51		
	82°·8 A		2·48		
	77°·3 A		2·22		
n-Propyl formate.	81°·0 A	79°·5 A	2·36	2·39	7·72
	77°·0 A		2·40		
	82°·6 A		2·44		
	77°·3 A		2·36		
n-Butyl formate.	82°·0 A	78°·7 A	2·45	2·43	—
	77°·0 A		2·42		
	77°·0 A		2·42		
Methyl acetate.	77°·3 A	77°·3 A	2·63	2·58	7·03
	76°·6 A		2·63		
	79°·0 A		2·60		
	77°·0 A		2·53		
	78°·0 A		2·53		
Ethyl acetate.	81°·0 A	79°·15 A	2·45	2·48	5·85
	77°·3 A		2·515		
n-Propyl acetate.	82°·8 A	80°·9 A	2·41	2·42	5·65
	82°·8 A		2·49		
	77°·0 A		2·44		
	81°·0 A		2·34		
n-Butyl acetate.	76°·8 A	77°·6 A	2·38	2·41	5·00
	78°·4 A		2·44		

The frequency of the oscillations used was throughout of the order of $4{\cdot}7 \times 10^5$ per sec.

It will be seen from the above tables that the values of the dielectric constants of these esters when measured at the temperature of liquid air are throughout considerably less than the values obtained at ordinary temperatures. These low values are characteristic of the solid state, for the general course of the change of the dielectric constant with decrease of temperature is first an almost linear rise of the value of the constant as the temperature falls until the melting-point is reached, then a sudden fall during solidification to a value less than that obtained at ordinary temperatures, then a very slow rise as the temperature is further decreased. This phenomenon is illustrated by the case of n-butyl acetate, for which the results obtained for the dielectric constant throughout the range of temperature 292° A–80° A are given below. That this is probably a general phenomenon is shown by the work of several investigators, as, for example, that of Abegg and Seitz on p-azoxyanisole (*Zeitsch. Phys. Chem.* xxix. p. 491, 1899) and various alcohols (*iid.* xxix. p. 242, 1899). This almost linear rise in the value of the dielectric constant with decrease in temperature is in agreement with the theory of the temperature variation of this constant put forward by Debye (*Phys. Zeit.* xiii. pp. 97–100, Feb. 1, 1912) on the basis of the assumption of the presence of "dipoles" in the liquid dielectric.

Returning to the tables, it will be seen that, though the values of the dielectric constants at ordinary temperatures of the corresponding members of the series of formates and acetates are distinctly different, they become approximately equal at low temperatures. This would seem to show that at these low temperatures the acid radicle contributes very little to the value of the dielectric constant.

An inspection of the table will also show that the ratio of the dielectric constant of any member of either series to that of the next higher member does not remain throughout the series the same at low temperatures as it is at ordinary temperatures.

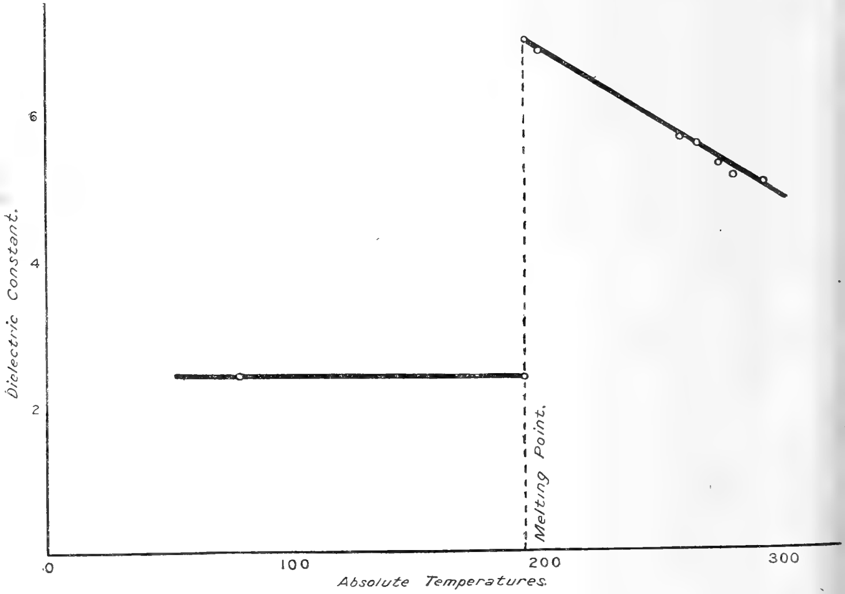
In Table II. are given the results obtained for the case of n-butyl acetate for the range of temperature 292° A–80° A. The temperatures were obtained by surrounding the vessel holding the experimental condenser by air (292° A), ice (273° A), freezing mixture (264°·5 A–258°·7 A), solid CO_2 and ether (200°·5 A), and liquid air (77°·6 A). Readings were taken at each of these temperatures, the results in the table being mean values. Readings were also obtained when the n-butyl acetate was just beginning to solidfy and when it was solid just below the melting-point. The melting-point was afterwards determined, the result obtained being −77°·9 C.

TABLE II.

n-Butyl acetate.

Temperature.	Dielectric Constant.
292° A	5·05
280°·5 A	5·10
273°·5 A	5·25
264°·5 A	5·59
258°·7 A	5·625
200°·5 A	6·85
195°·1 A just melting.	6·965
195°·1 A just solid.	2·395
77°·6 A	2·41

Fig. 2.



The results are plotted graphically in fig. 2. It will be seen that the dielectric constant arises from 5·95 at 292° A to 6·965 at 195°·1 A, the melting-point, in a manner such that the relation of the dielectric constant to the temperature is almost exactly a linear one. Then there is a sudden fall in the value during solidification to 2·395, and finally a very small rise to 2·41 at 80° A. The present arrangement did not permit of an accurate determination as to whether there was an actual discontinuity in the value of the dielectric constant at the melting-point, or whether the change took place in a small range of temperature. The former alternative is probable, and the change is so represented in the graph (fig. 2).

Summary.

A method is described for the determination of the dielectric constants of liquid or solid substances by the aid of triode valve circuits. The results obtained by this method for the dielectric constants of methyl, ethyl, n-propyl, and n-butyl formates, and the corresponding acetates at the temperature of liquid air, are then given and compared with the values obtained by other investigators at ordinary temperatures. It is shown that at the low temperatures the acid radicle apparently contributes but little to the value of the dielectric constant. Results showing the dependence on temperature of the dielectric constant of n-butyl acetate throughout the range of temperature 292° A–80° A are also given. It is found that the dielectric constant of this substance increases linearly with decrease of temperature down to the melting-point, at which a sudden fall in the value occurs, followed by a very gradual rise as the temperature is further lowered.

The author desires to express his indebtedness to Prof. E. H. Barton, F.R.S., for the facilities afforded to him in his laboratory, to Mr. C. F. Ward, B.Sc., for his kind assistance in the rigorous purification of the materials used, and to the Department of Scientific and Industrial Research for a grant by the aid of which the above work was carried out.

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LV. *A Study of Franklin's Experiment on the Leyden Jar with Movable Coatings.* *By* G. L. ADDENBROOKE, *M.I.E.E.*[*]

TO understand the actions in dielectrics it is very desirable to have a clear idea of the principles which underlie electrostatic actions. For the most part these can be found in text-books, but there is one respect in which they are all defective, and that in connexion with one very

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[*] Communicated by the Author.

important action which bears largely on a class of problems which has much practical importance.

This is known as the "Franklin Experiment" on the Leyden Jar with movable coatings.

The experiment in its simplest form is briefly thus:—The jar is charged, the inner coating is lifted out by an insulated hook, and this inner coating is then touched against the outer coating and put back. It is found that when taken out the inner coating carries scarcely any charge, and that when it is put back a full or nearly full discharge can be got from the reconstituted jar.

The experiment is sometimes varied by placing the charged jar on an insulating stand and taking away by insulated tongs both the covers, leaving the glass jar exposed. Both covers are found to be practically uncharged, they are then touched against each other. The whole jar and coatings are next reconstituted, when a full discharge can be obtained.

This has been taken to mean that when a dielectric between two electrodes is charged, if the electrodes are taken away while still charged, the energy of the charge is left stored in the dielectric, and remains there until the electrodes are restored and short-circuited, or the charge dies down by some indefinite form of leakage.

For a long time I could not reconcile this experiment and its general interpretation with the views I had been led to form of electrical actions in dielectrics in other respects. I therefore searched through a number of works for the purpose of finding any variations there might be in the methods of performing the experiment, or in the explanation of it, when I noticed that there seemed to be no mention of it in Faraday's or Maxwell's work. It is not mentioned in Gordon's 'Electricity and Magnetism,' nor in Sir J. J. Thomson's Text-book, though it is described in Poynting and Thomson's 'Electricity and Magnetism' of 1914. This was significant, though it seemed almost equally significant that if the experiment was omitted for any reason, no reasons should be given for so doing.

At last, to clear up the matter there seemed no other course but to investigate it further oneself.

In considering how to do this the first point which struck me was that a glass jar was invariably mentioned as the dielectric.

The question arose what would happen if another dielectric were substituted.

Finally, solid paraffin was selected as a suitable substitute on account of its high insulating properties, and because its surface is not so hygroscopic as glass. After some trouble I succeeded in casting a thin but perfect jar of paraffin fitting the same metal coatings as a glass jar I had.

The usual experiment was tried with this, but instead of charging the jar from an electrical machine, the jar was connected to a gold-leaf electroscope, and charged from an electrophorus.

By this method one does not need such high potentials, there is less loss from leakage, and it is possible to see what is going on and make approximate quantitative measurements.

In this way the jar was charged to 500–600 volts, and the deflexion on the electroscope noted. The inner coating of the jar was then lifted out by an insulating handle, touched to the outer coating and replaced. It was then re-connected to the electroscope. Contrary to the case with the glass jar there was no appreciable charge remaining in the jar; in fact, repeated experiment showed that on lifting out the inner coating and earthing it, or connecting it to the outer coating, the dielectric was completely discharged in the act, and only the barest trace of charge remained when the inner coating was put back. Also the charge evidently came away on the inner metallic coating when it was lifted out, as could be plainly seen on the electroscope. In fact, the action was exactly the reverse to the account of it usually given. On the other hand, the actions as now found seemed completely in accord with the Faraday-Maxwell theory, and with known electrostatic laws. Briefly they showed, that the action on the dielectric is inductive, that if the inner charged electrode were brought outside, the lines of force going to the outer electrode no longer went through the dielectric, which accordingly lapsed to its normal and neutral state.

If when the jar with paraffin dielectric is charged it is placed on an insulated stand and both coatings are taken off by insulated handles, both coatings will be found to have strong and equal charges of opposite signs. If these two coatings are then touched together, and the jar is reconstituted, it will be found to have no charge as before.

Having thus clearly shown that there is a difference in the results of the experiment when glass is used and a better dielectric such as paraffin, I determined to vary the glass experiment as follows:—The glass jar was first thoroughly warmed. It was then put in a large dry cupboard, and kept dry for a couple of days by means of plenty of calcium chloride.

This dry cupboard is so arranged that, by means of oil silk sleeves passing through holes in one of the sides, and wearing rubber gloves, one can manipulate inside without introducing moisture.

The Franklin experiment with glass dielectric was then repeated with the dried glass in a thoroughly dried atmosphere.

The effects observed were now no longer the same as before, but were the same as described with the paraffin jar. That is, after charging and taking out the inner coating and touching it to the outer coating and replacing, there was only a slight charge remaining, due doubtless to absorption. For all practical purposes the characteristic actions as described in the text-books were wanting, and the results come in line with the Faraday-Maxwell theory.

It is clear from other experiments I have made (see Physical Society's Proceedings, 1912) that, in the case of the glass jar, condensed moisture on its surface is under all ordinary circumstances sufficient to form a semi-conducting film, of high resistance, but sufficiently conducting for the charge on the electrodes to escape to it when one is removed, or before, especially as when the experiment is tried under conditions as above, the electroscope shows that if the electrodes are separated the same action takes place as when the cover is removed from an electrophorus, that is as the electrodes are separated their difference of potential rapidly increases.

This is more the case as the dielectric constant of glass is so high that the slope of the potential is chiefly concentrated on and is very great across any small air space between the glass and the electrodes.

A small motion of the electrodes already charged to a fairly high potential, therefore, raises this potential at least two or three times so that there is a strong tendency for the charge to flow to the glass surface, even if there is only momentary contact at two or three points.

I have related my work on this experiment at some length because it became more and more clear to me that to arrive at any clear understanding of the actions of electric fields on dielectrics, the correct interpretation of the experiments is essential.

It has always appeared to me that this experiment was about the most striking and most fundamental in all the realm of electrostatics. It seemed so convincing that for many years I, and I know numbers of others, have accepted it and still do without question, as ordinarily interpreted.

It is such a striking experiment that when I began to doubt its interpretation it appeared to me that to leave it without rational explanation left a fundamental point in an undecided state, as there was no other experiment which gave an equally convincing demonstration of the real actions.

In drawing attention to this matter I trust it may not lead to teachers abandoning the experiment, as it is now omitted in some cases. As reconstructed, besides demonstrating the main theoretical point, it brings into prominence the other actions, and coordinates these actions with the behaviour of the electrophorus and other electrostatic facts, while it also draws attention to the question of leakage and surface effects which are very indefinitely understood at present but which are being found increasingly important.

Instead of being tried only with a glass jar I would suggest that the experiment be tried also with a high-class ebonite jar, which would be less fragile than paraffin, as I think it would succeed if the ebonite was kept in the dark in a closed glass jar with calcium chloride up to the moment of use. It is difficult to speak definitely of glass, its surface state varies so, but I think in most cases if the experiment were tried as usual, and then the glass jar were heated to 100° C. and kept over calcium chloride for 20 minutes till it was cold, if the experiment was then quickly made in the open air, it would be found to fail from the Franklin point of view, although it succeeded well in the first trial.

LVI. *A New Model of Ferromagnetic Induction. By* Sir J. Alfred Ewing, *K.C.B., F.R.S., Principal of the University of Edinburgh* [*].

I HAVE lately reconsidered, in the light of what is now known about atomic structure, the theory of induced magnetism in iron and other ferromagnetic substances which I put forward more than thirty years ago, and have come to see that it needs substantial amendment. A new model of the process of ferromagnetic induction has to take the place of the model then suggested. The new model is the subject of a recent communication to the Royal Society (Proc. Roy. Soc. Feb. 1, 1922), but a brief account may be offered to the Philosophical Magazine, in which the model of 1890 was described on its first introduction [†].

The revised theory and the new model retain this fundamental feature, that there is in every ferromagnetic atom a Weber element possessing magnetic moment and capable of

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[*] Communicated by the Author.

[†] Phil. Mag., 5th series, vol. xxx. p. 205 (Sept. 1890).

being turned into alignment by a sufficiently strong external field, and that the control of the Weber elements—which resists their turning and gives rise to the phenomena of hysteresis—is due entirely to magnetic forces. When they are caused to turn there is first a small stable deflexion, then a breaking away from the position of stability and a falling over, through an unstable phase, into a new position of stability. In this essential characteristic the new model resembles the old one. But in the old model the only magnetic forces that contributed to the control of any one Weber element were the forces between it and other Weber elements. In the new model a great part of the magnetic control is due to forces between the Weber element and other portions of the same atom. The Weber element—the thing that turns—is probably only a small part of the atom *.

Before describing the new model it is necessary to point out in what respect the old one fails. The old model consisted entirely of pivoted magnets which represented the Weber elements in the atoms of a crystal, say of iron. Their mutual magnetic forces made them form rows. When a weak external field was applied, the magnets in any row that lay more or less transverse to it underwent a small stable deflexion, corresponding to the initial stage of magnetization which the late Lord Rayleigh showed to be quasi-elastic. When the field was sufficiently increased the rows broke up and other rows were formed in a more favourable orientation. This corresponds to the "steep" stage in the magnetizing curve. Now it is known that in ordinary iron barely one per cent. of the whole magnetism of saturation is acquired in the quasi-elastic stage before the effects of hysteresis set in. To conform to this condition, the magnets of the model must have only a very narrow range of stable deflexion, and consequently they have to be set very near together, with the result that in the old model their mutual control became excessive. A calculation of the force required to break up rows of pivoted magnets, of atomic dimensions, when set near enough together to satisfy the above condition, showed it to be many thousands of times greater than the force which is actually required, in iron, to reach the steep part of the curve. The original model, therefore failed quantitatively, and a model had to be sought for which would exhibit similar qualitative features but would provide a far weaker control, while still allowing no more than a very narrow range of stable deflexion. This is arrived at as follows.

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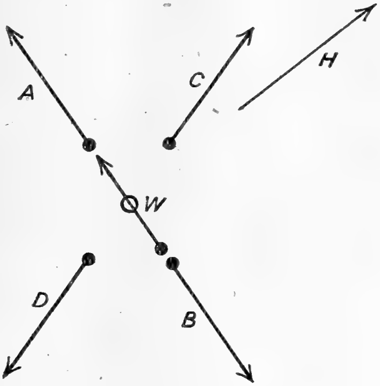
* *Cf.* A. H. Compton and O. Rognley, Phys. Rev. xvi. p. 464 (1920).

Let W, fig. 1, be a pivoted magnet controlled by two fixed magnets A and B, which point in opposite directions.

Assume, in the first instance, that the attracting pole of A acts on W somewhat more strongly than the repelling pole of B, so that there is a feeble control due to this difference. Assume further that the clearance between W and the adjacent poles of A and B is very small. Let an external field H be applied. Then as H is increased W will deflect stably through a small angle, however nearly balanced are the forces of control exerted by A and B. When the deflexion exceeds a certain small angle, W becomes unstable.

Fig. 1.

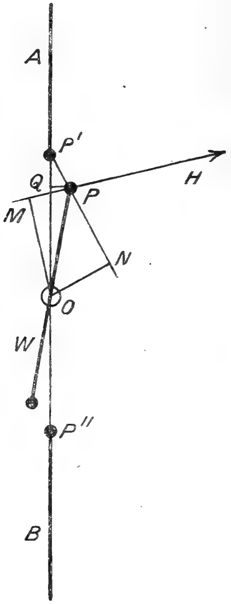


If there is a second pair of fixed magnets placed as at C and D, W will tend to assume a stable relation to them, but a further increase of H will make it break away from their control also into a position nearly parallel to the field. To make such a model completely imitate the process of ferromagnetic induction we have only to think of it as extended into three dimensions, letting W be pivoted with two degrees of rotational freedom, and surrounding it by say four pairs of fixed controlling magnets, situated on the four diagonal axes of a cube. The sketch, drawn for a diagonal plane, shows two such pairs. It is obvious that if a substance were made up of atoms on this model all the familiar characteristics of ferromagnetic induction would be reproduced in it when a field was applied, removed, reversed and so on, or when the piece was made to rotate in a constant field. Since the strength of the control may be reduced to any desired extent, a quantitative agreement with the results of experiment becomes possible.

To examine the conditions which determine the range of stable deflexion, let m be the pole-strength at each end of W, and m' and m'' be the pole-strengths of A and B respectively. Assume the clearance to be the same at both ends of W. Write r for OP (fig. 2) the half length of W, a for OP′, x for PQ and c for PP′.

Let the field H act with a constant inclination α to the line of centres, deflecting W stably through an angle θ. In what follows the angle θ is assumed to be very small.

Fig. 2.



Then for the pole P the deflecting moment due to the action of H is $m\mathrm{HOM} = m\mathrm{H}r\sin(\alpha-\theta)$, and the restoring moment due to P′ is

$$\frac{mm'}{c^2}\,\mathrm{ON} = \frac{mm'\,ax}{c^3}.$$

Hence, taking both poles of W into account, but neglecting effects of other than the nearest fixed poles, the equation of equilibrium is

$$2m\mathrm{H}r\sin(\alpha-\theta) = \frac{m(m'-m'')ax}{c^3},$$

or

$$\frac{2\mathrm{H}r}{a(m'-m'')} = \frac{x}{c^3\sin(\alpha-\theta)}.$$

It follows that as H is increased, the limit of stable deflexion is reached when

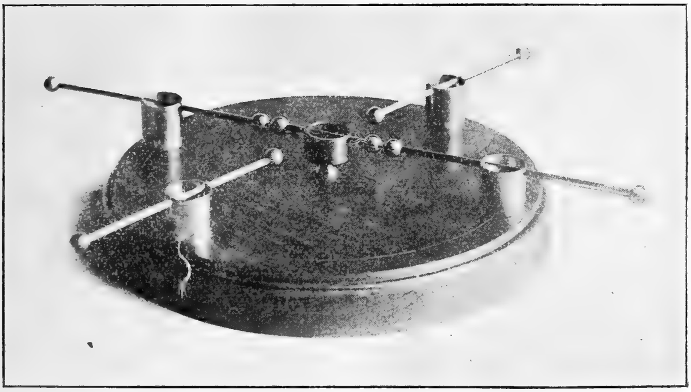
$$\frac{d}{dx} \cdot \frac{x}{c^3 \sin(\alpha-\theta)} = 0.$$

We are concerned only with a very narrow range of stability, and it will simplify the expression if we confine it to cases in which $\sin(\alpha-\theta)$ may be treated as sensibly equal to $\sin \alpha$, cases namely in which θ is very small and α is not small. Under these conditions the criterion for rupture becomes

$$\frac{d}{dx}\left(\frac{x}{c^3}\right)=0,$$

which gives $x = \frac{a-r}{\sqrt{2}}$, since $c^2=x^2+(a-r)^2$. In other words the deflexion ceases to be stable when the angle OP′P becomes $\tan^{-1}\frac{1}{\sqrt{2}}$ or 35° 16′. The criterion is a geometrical one: it is independent of the strength of the control, which depends on $m'-m''$. A narrow range of stable deflexion is retained by keeping the poles near together, though the strength of the control may be made vanishingly small.

Fig. 3.



A model illustrating these points is conveniently made as in fig. 3, using straight pieces of steel wire with ball ends for the magnets. The central magnet is pivoted on a needle and carries a vertical piece of brass tube to give it gravitational stability. The fixed magnets are held in supports which admit of adjustment for direction, height, and nearness to the centre. When equally strong fixed magnets are chosen and the clearances are made equal, the model always shows some magnetic stability, for the distribution of magnetism in the wires is slightly altered by induction, with the effect of bringing the unlike poles at one end nearer together, and driving the like poles at the other end further apart. When the pivoted magnet is made to turn round from one pair of fixed magnets to another it exhibits this stability in each successive position.

Consider next how the parts which make up the model may be thought of as having equivalents in the structure of the atom. It would seem that the electrons of each atom, which possess magnetic quality through rotating in orbits, or perhaps through being rings, furnish two types of magnetic element, a turning element near the nucleus and other elements at a greater distance from it, which are held fixed—more or less completely—in consequence of the forces between the atom and its neighbours in the crystal. A. W. Hull has shown by his X-ray analysis that the space-lattice of iron is the centred cube, and has suggested as a probable structure for the iron atom one in which two of the electrons form a doublet, with the nucleus in the middle, and the remaining twenty-four electrons are grouped in octets, further out along the diagonals of a cube [*]. On the basis of this suggestion, we may think of these octets as supplying the four pairs of magnetic elements which correspond to the fixed magnets A, B, C, D, etc., of the model, with axes that lie along the cube diagonals of the atom (presumably coinciding with the trigonal axes of the crystal). They point radially inwards, and in any one atom all their inner "poles" are of the same name. In the inner space a group, possibly the doublet, which may be taken to constitute the Weber element and corresponds to W of the model, turns in response to an impressed field. So long as there is no impressed field the Weber element may be in any one of eight positions of stability, pointing towards one of the fixed elements. Its small reversible deflexion before breaking away constitutes the quasi-elastic stage that is found when one begins to magnetize or to change from an increasing to a diminishing field, or *vice versa*. Its irreversible passage from one position of stability to another is what makes hysteresis. In a substance such as soft iron there is no more than a narrow range of stability because the clearance is small; and the control which gives stability

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[*] "The Crystal Structure of Iron," Phys. Rev. ix. p. 85 (1917).

is weak because it depends on a nearly perfect balance between forces that exert opposing moments, though these forces are separately strong.

Suppose, as an ideal case, that the opposing actions within the atom are exactly balanced: in other words that each Weber element turns between fixed elements which exert precisely equal magnetic forces on its poles. In that extreme case it will still be stable when the atom stands as one of a row of atoms in the crystal. For the Weber elements in the successive atoms of the row will still exert mutual forces on one another—across a relatively large gap—and will tend, as in my model of 1890, to set themselves in a row. Their mutual action will give them a stability which is feeble because of their wide spacing; but there will be this important difference from the model of 1890, that the presence of fixed magnets in the gap, though by hypothesis it contributes nothing to the resultant stability, limits the range of stable deflexion.

It is open to conjecture that in an ideal crystal of perfectly pure and perfectly unstrained iron the action of the fixed magnets may be perfectly balanced, and remain balanced when the Weber element turns. In that case the stability of the Weber elements would be due only to the forces which they exert on one another from atom to atom. On the other hand, there may be even in pure unstrained iron an excess in the force between unlike poles over the force between like poles. There may be an action such as occurs in the model with steel magnets, by which the Weber element itself disturbs this balance, with the result that the unlike poles attract more strongly than the like poles repel. In that case the Weber element would be stably held by the fixed magnets of its own atom, when in line with any pair. As it turns it transfers to the pair between which it lies a slight inequality of forces on which its stability depends.

In any event it is probable that the atom is capable of distortion, and is in fact distorted when the piece is strained. It is well known that a homogeneous ferromagnetic metal becomes magnetically æolotropic under strain. The model suggests that such an effect is due to the setting up of differences in the closeness of the controlling magnets along different axes. Extreme amounts of straining, such as those that are experienced when a non-crystalline state is produced (as in the experiments of Beilby)—with atoms forced out of their places in the lattice—are probably associated with considerable distortion of the atoms. We should expect this to disturb the balance of opposed magnetic forces, but unequally in different atoms, with the effect of irregularly augmenting the control, so that the metal becomes much less easily magnetized and the curve of magnetization assumes a more rounded form with less sharply separated stages, as is in fact observed. Similarly, when atoms of foreign matter have to find places in the space-lattice the symmetry of the neighbours will be affected, and we may expect the Weber elements in them to be in consequence unduly stabilized. This is borne out by the fact that the hysteresis of iron becomes in general less and its susceptibility greater the more completely all impurities are eliminated. Again, in a chemical compound of a ferromagnetic metal, say iron, the distortion of the iron atom which comes of its being unsymmetrically surrounded may cause its magnetic properties to differ widely from those of an atom of uncombined iron, and may be associated with the magnetic æolotropy which is conspicuous in the crystals of certain compounds.

The form of model described above is based on the Lewis-Langmuir type of atom. It is appropriate if the electrons are conceived to have orbits that are small in relation to the size of the atom, or to be small rings. But the same principles may be equally well embodied in a model that is based on the Bohr type of atom, with large electron orbits. The conditions to be satisfied are these: that a turning part, made up of one or more of the orbits with an unbalanced magnetic moment, should be capable of orientation by an impressed field, but under magnetic controls exerted by other parts of the atom, which are held relatively fixed; that it should deflect through no more than a very small angle before becoming unstable; that it should then fall over with dissipation of energy into another position of stability; and further that the stability in each stable position should be weak. These conditions are satisfied when the control depends on a balance of strong but oppositely directed moments. They are realized in the model of figs. 4 and 5.

There A and B (fig. 4) represent coplanar elliptic orbits with a common focus at the nucleus of the atom, which is also the centre of a circular orbit W representing the Weber element. The plane of A and B is to be thought of as fixed; the plane of W may turn. In the model (fig. 5) the elliptical controlling coils which correspond to A and B are set as nearly as may be in one plane, and W is a circular coil pivoted about a diameter *ab*. A margin of stability can be given by making one of the fixed coils act rather more strongly than the other. When the clearances at the sides of W, between it and the fixed coils, are small, its limit of stable deflexion is very narrow. The model is of course to be understood as having a second pair of similar controlling coils set in a transverse plane, and it is easy (in imagination) to extend the construction to three dimensions, adding other pairs of elliptical coils and supposing W free to turn about any axis in its own plane. Here a single electron orbit suffices to constitute the Weber element. It is interesting to find that all the main characteristics of ferro-magnetism are capable of representation by means of models which embody the same ideas in two widely different forms, based respectively on the two conceptions of atomic structure which physicists and chemists are endeavouring to reconcile.

Fig. 4

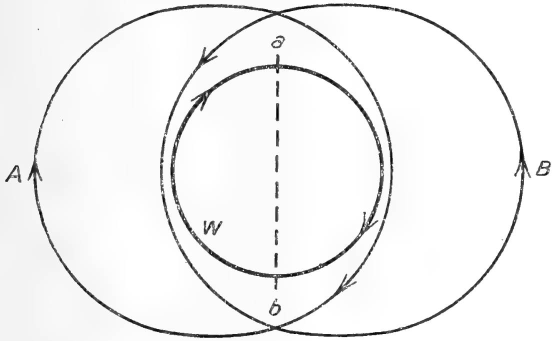
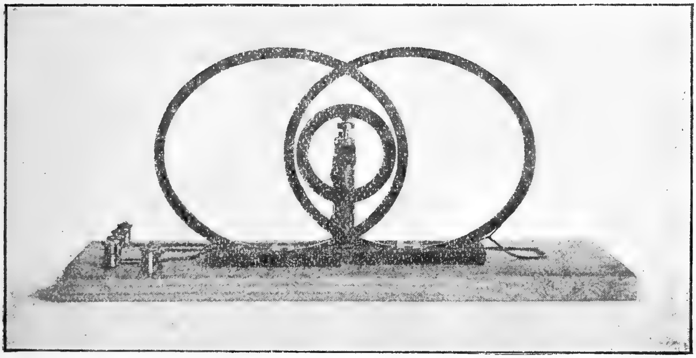
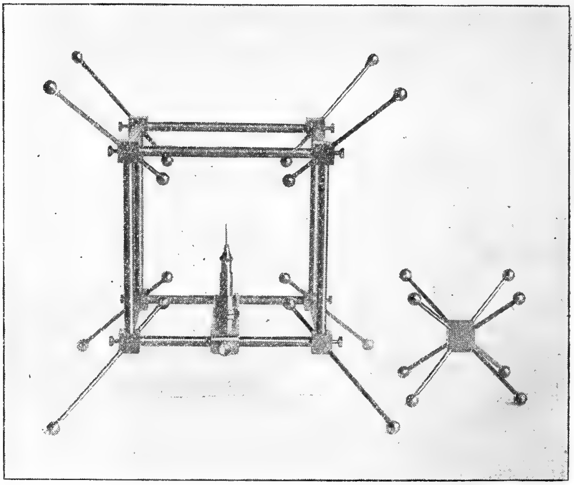


Fig. 5.



Though in these models the turning part has, for the sake of simplicity, been represented by a single coil or a single magnet, it will be obvious that in developing the theory here outlined the Weber element of a ferromagnetic atom may be regarded as possibly comprising a complex group of electron orbits, capable of turning as a whole within the outer system, or even more than one such group. Reverting to the model of fig. 1, where there is an octet of fixed magnets, namely the four that are shown in the sketch and other four in a plane perpendicular to that of the paper, the Weber element might itself have eight magnetic poles, placed at the corners of a cube and capable of turning as a rigid system about the centre. Such a model is conveniently made by using, for the part that turns, a cubic steel boss with projecting magnets screwed into its eight corners in the direction of the diagonals of the cube, and magnetized so that four of the projecting poles have one polarity and the four opposite poles have the other polarity. In fig. 6 the eight fixed magnets are held in a skeleton cube of brass rods, and the octet which forms the Weber element is, for the sake of clearness, removed from its place on the pivot and shown separately. When the model is arranged in this form it is practicable to reproduce conditions of extreme magnetic æolotropy. Thus we may advance one pair of opposite fixed magnets (in the outer shell) until

Fig. 6.



they touch one pair of opposite magnetic poles in the turning part which represents the Weber element, with the result that one of its axes becomes fixed and rotation can consequently occur only about that axis. The magnetic properties of the model system then resemble those of pyrrhotite, a crystal of which, as Weiss * showed, will take up magnetic induction readily in one plane, but not in the direction perpendicular to that plane. The model may also be adjusted to exhibit differences of magnetic quality along different axes in the plane of magnetization. Such differences were in fact observed in pyrrhotite by Weiss. He found that when a crystal was turned about its non-magnetic axis in a fixed field there were abrupt magnetic changes at intervals of 60°. This is just what a study of the model would lead one to expect, for the projecting magnets in the turning element lie in planes 60° apart round any one of its magnets taken as axis. Periodic variations along axes inclined at 120° to one another in the plane of easy magnetization are consistent with cubic symmetry on the part of the iron atom: they follow directly from the assumed grouping of magnet poles at the corners of a cube. And they will occur at intervals of 60° if we ascribe the hexagonal structure of the crystal to twinning in successive layers.

If Hull's view of the structure of the iron atom be correct, it seems not improbable that the Weber element includes not only the duplet of electrons which he places near the nucleus, but also the innermost octet, the members of which are somewhat further away from the nucleus, leaving the other and more distant octets to constitute what I have called the fixed elements.

LVII. *On the Amplitude of Vibrations maintained by Forces of Double Frequency.* *By* N. C. KRISHNAIYAR, *M.A., Lecturer in Physics, University College, Rangoon* †.

LORD RAYLEIGH ‡ was the first to discuss the theory of the vibration maintained by an influence whose frequency was double that of the vibration maintained. A well-known example of such maintenance is the longitudinal form of Melde's experiment. His differential equation took the form

$$\ddot{y} + k\dot{y} + (n^2 - 2\alpha \sin 2pt)y = 0,$$

k and α being small quantities.

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* Weiss, *Jour. de Phys.* iv. p. 469 (1905).

† Communicated by the Author.

‡ 'Theory of Sound,' vol. i. pp. 81–85.

Assuming

$$y = A_1 \sin pt + B_1 \cos pt + A_3 \sin 3pt + B_3 \cos 3pt$$
$$+ A_5 \sin 5pt + B_5 \cos 5pt + \dots.$$

and equating to zero the coefficients of $\sin pt$ and $\cos pt$ in the relation obtained when this value of y was substituted in the differential equation, he showed that A_3 and B_3 were of the order α and therefore negligible relatively to A_1 and B_1. Hence as a first approximation,

$$A_1(n^2-p^2)-(kp+\alpha)B_1=0,$$
$$B_1(n^2-p^2)+(kp-\alpha)A_1=0.$$

Therefore

$$\frac{B_1}{A_1}=\frac{n^2-p^2}{kp+\alpha}=\frac{\alpha-kp}{n^2-p^2}=\frac{\sqrt{\alpha-kp}}{\sqrt{\alpha+kp}}$$

and $\quad (n^2-p^2)^2=\alpha^2-k^2p^2.$

According to this theory, the phase $\tan^{-1}B_1/A_1$ is constant and independent of the amplitude maintained, and the amplitude $\sqrt{A_1^2+B_1^2}$ is indeterminate. But it is known * experimentally that the phase of the vibration is not independent of the amplitude, and a study of the maintained amplitudes brings out a number of results which the above theory does not indicate.

In the case of fork maintenance the vibration of the wire reacts on the vibration of the fork and alters the amplitude of the latter, and so a difficulty arises in interpreting the results observed. The author † found that when an alternating current of 50 cycles, and therefore of 100 heat cycles, was passed through a wire whose length and tension were adjusted to a frequency of 50, the wire on account of the periodic thermal expansion vibrated with a large amplitude. The effect of the earth's magnetic field was found to be negligible, the experiment succeeding equally well in all positions of the wire including the position when the wire was along the direction of the earth's magnetic force. The periodic thermal expansion due to the alternating current heating being independent of the vibration of the wire, there is no reaction between the vibrating system and the

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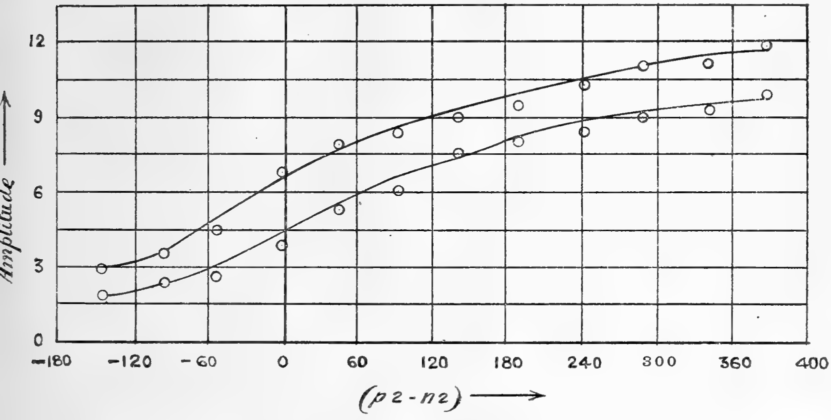
* C. V. Raman, Physical Review, December 1912, pp. 451–453; N. C. Krishnaiyar, Physical Review, December 1919, pp. 494–496: R. N. Ghosh, Proc. Indian Assoc. Cultivation of Science, vol. vi, pp. 75 & 84 (1920).

† N. C. Krishnaiyar, "On the maintenance of vibrations of wires by electric heating," Physical Review, n.s. vol. vi. no. 6.

maintaining influence. There is no mechanical force acting at a node or any other point of the wire. Hence a strict comparison of the observed amplitudes with theory is possible.

It is the aim of this paper to develop the theory so as to explain the facts of observation regarding the amplitude maintained. The details of the experiment are given in the paper cited above, and it will suffice to summarize below the main results. α is the constant factor of the periodic maintaining influence and in the experiment, for the same wire, depends upon the current through the wire and can be kept constant for an indefinite length of time or can be altered at will. n is the natural frequency of the vibrating wire, and can be altered by altering the tension or the length of the wire, It was found that the maintenance started when the tension was slightly greater than that necessary to make $n=p$, i. e. when p^2-n^2 was negative. Maintenance continued as tension diminished so as to make $n=p$ and n less than p, i. e. as p^2-n^2 became zero and as p^2-n^2 increased positively.

Fig. 1.



(1) When the observed amplitudes are plotted * against the differences of the squares of the forced and the natural frequencies, there is no "peak" or maximum resonance as in the case of the ordinary forced oscillations, but only a continual increase in the amplitude from one end of the range where p^2-n^2 is negative to the other end of the range where p^2-n^2 is positive.

(2) The amplitude increases to a maximum value after

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* Figure 1 of the author's paper cited above.

which any diminution of tension brings about a sudden collapse of maintenance.

(3) The amplitude graph though parabolic in parts is not continually so; the arc at one end produced parabolically does not coincide with the arc at the other end but is nearly parallel.

(4) The maximum amplitude maintained increases if α increases in value.

(5) There is a lower limit to the value of α for maintenance to happen.

(6) There is an upper limit to the value of the excess tension, *i. e.* an upper limit to the magnitude of p^2-n^2 when $n>p$ if maintenance should happen. Beyond this, there is no vibration of the wire at all. The projection of the wire by a magic-lantern on a distant screen remains a sharp image.

(7) This upper limit to excess tension increases with increase of α. In other words, when α is larger, maintenance starts with a larger excess tension.

Most of the observations detailed above have been confirmed by R. N. Ghosh * by an entirely different method of maintenance, viz. by means of an electric motor vibrator originally designed by J. A. Fleming and subsequently improved by C. V. Raman †.

In the theory developed below, a term βy^2 is introduced in the part of the equation representing tension to denote the variation proved ‡ experimentally to occur in free oscillations of sensible amplitude. This variation is due to the second order differences in length between the equilibrium position and the displaced position of the wire and is proportional to the square of the displacement. The frictional force is put down as the sum of two terms, one proportional to the velocity and the other proportional to the square of the velocity. Ordinarily, as Sir G. G. Stokes has shown, the frictional force is proportional to the velocity when the velocity is small, and proportional to the square of the velocity when the velocity is relatively large. This apparent change of the law of friction with increase of velocity can be explained by the assumption that the frictional force always consists of two terms, the first term proportional to the velocity and the second term proportional to the square of the velocity, the coefficient of velocity being relatively larger

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* Proc. Indian Assoc. 1920, vol. vi.

† Physical Review, November 1919.

‡ C. V. Raman, "Photographs of vibration curves," Phil. Mag. May 1911: Physical Review, December 1912.

than the coefficient of the square of the velocity. When the velocity is small the first term will be the dominating term, and as the velocity increases, the second term will increase more rapidly than the first and will become ultimately the dominating quantity. Froude * has shown that the forced oscillations of a ship rolling among waves are due to a periodic forcing cause damped by resistance varying with both the first and the second powers of the angular velocity. Routh † has shown analytically that the period of a pendulum in a very rare medium resisting partly as the velocity and partly as the square of the velocity, is constant throughout the motion and independent of the arc. Parker Van Zandt ‡ has shown experimentally that the free vibrations of a system with a resisting torque due to both first and second power damping are isochronous. This law of frictional force when introduced into the differential equation brings out all the above facts of experiment in double frequency maintenance.

The differential equation may be written as

$$\ddot{y} + k'\dot{y} \pm k\dot{y}^2 + (n^2 - 2\alpha \sin 2pt + \beta y^2)y = 0.$$

The sign $\pm$ is introduced in the third term to indicate that that part of the frictional force changes sign as velocity changes sign.

Assume as before,

$$y = A_1 \sin pt + B_1 \cos pt + A_3 \sin 3pt + B_3 \cos 3pt$$
$$+ A_5 \sin 5pt + B_5 \cos 5pt + \ldots,$$

and consider in the limit all coefficients other than A_1 and B_1 to be negligible. Collect the coefficients of $\sin pt$ and $\cos pt$ with the aid of the following relations:

$$y = A_1 \sin pt + B_1 \cos pt + \ldots.$$
$$\dot{y} = p(A_1 \cos pt - B_1 \sin pt) + \ldots.$$
$$y \sin 2pt = \tfrac{1}{2}(A_1 \cos pt + B_1 \sin pt) + \ldots.$$
$$y^3 = \tfrac{3}{4}A_1(A_1^2 + B_1^2) \sin pt + \tfrac{3}{4}B_1(A_1^2 + B_1^2) \cos pt + \ldots.$$

The above are easily obtained by differentiation and trigonometric transformation.

$$\dot{y}^2 = p^2(A_1^2 + B_1^2) \cos^2 (pt + \tan^{-1} B_1/A_1).$$

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* Sir Phillip Watt's article on Shipbuilding in the *Encyclopædia Britannica.*

† Routh's 'Advanced Rigid Dynamics,' Art. 364.

‡ J. Parker Van Zandt, Physical Review, November 1917.

Expanding the even function $\cos^2(pt+\tan^{-1}B_1/A_1)$ by Fourier's Series into a series of cosines of multiples of $(pt+\tan^{-1}B_1/A_1)$ between the limits $-\frac{\pi}{2}$ and $\frac{\pi}{2}$, the term containing $\cos(pt+\tan^{-1}B_1/A_1)$ is obtained as

$$\frac{8}{3\pi}p^2(A_1^2+B_1^2)\cos(pt+\tan^{-1}B_1/A_1),$$

and it can be written as

$$\frac{8}{3\pi}p^2A_1\sqrt{A_1^2+B_1^2}\cos pt-\frac{8}{3\pi}p^2B_1\sqrt{A_1^2+B_1^2}\sin pt.$$

Equating the collected coefficients of $\sin pt$ and $\cos pt$ separately to zero, we obtain

$$A_1\{n^2-p^2+\tfrac{3}{4}\beta(A_1^2+B_1^2)\}$$
$$=B_1\left\{\alpha+\left[pk'\pm\frac{8}{3\pi}p^2k\sqrt{A_1^2+B_1^2}\right]\right\}$$

and

$$B_1\{n^2-p^2+\tfrac{3}{4}\beta(A_1^2+B_1^2)\}$$
$$=A_1\left\{\alpha-\left[pk'\pm\frac{8}{3\pi}p^2k\sqrt{A_1^2+B_1^2}\right]\right\}.$$

Therefore

$$\{n^2-p^2+\tfrac{3}{4}\beta(A_1^2+B_1^2)\}^2=\alpha^2-p^2\left[k'\pm\frac{8}{3\pi}pk\sqrt{A_1^2+B_1^2}\right]^2.$$

If A stands for the amplitude of the maintained vibration,

$$\sqrt{A_1^2+B_1^2}=A.$$

$$\therefore\quad\{\tfrac{3}{4}\beta A^2-(p^2-n^2)\}^2=\alpha^2-p^2\left[k'\pm\frac{8}{3\pi}pkA\right]^2.$$

(1) The amplitude A is not symmetrical with respect to p^2-n^2. So there will be no "peak" or maximum resonance. The last term on the right involving the squares and product of the small quantities k and k' will be of small importance in the change of the value of A. So the relation between A and p^2-n^2 will be nearly parabolic.

(2) Since the right-hand side $\alpha^2-p^2\left[k'\pm\frac{8}{3\pi}pkA\right]^2$ is equal to a square and therefore cannot be negative, the

magnitude of A cannot be greater than $\frac{3\pi}{8p^2k}(\alpha-pk')$. Increase of p^2-n^2 above the value required to give this maximum value of A renders A imaginary. Hence a collapse of maintenance occurs.

(3) Substitute for $\frac{3\pi}{8p^2k}(\alpha-pk')$ the symbol A_m denoting maximum maintained amplitude.

Then

$$\left\{\tfrac{3}{4}\beta A^2-(p^2-n^2)\right\}^2=\alpha^2-\left\{pk'+(\alpha-pk)\frac{A}{A_m}\right\}^2.$$

At the excess-tension end, A/A_m is very small and if neglected the graph reduces to the form

$$\tfrac{3}{4}\beta A^2=\sqrt{\alpha^2-p^2k'^2}+(p^2-n^2);$$

and at the defect-tension end, A/A_m reduces to unity and the graph to the form

$$\tfrac{3}{4}\beta A^2=p^2-n^2.$$

The two limiting forms differ only by a constant. This shows that the shape of the graph at the two extremes is similar.

(4) $$A_m=\frac{3\pi}{8p^2k}(\alpha-pk').$$

Therefore A_m increases if α increases in value.

(5) The least value of α necessary for maintenance is that which makes the expression for the maximum maintained amplitude just equal to zero. Since $A_m=\frac{3\pi}{8p^2k}(\alpha-pk')$, the lower limit of the value of α is pk'. Or since $\alpha^2-p^2[k'\pm 8/3\pi\, pkA]^2$ is equal to a square, the least value of α is $p(k'\pm 8/3\pi\, pkA)$, and since there is no maintenance, $A=0$ and the least value of α is pk'.

(6) At the excess-tension end, $\sqrt{\alpha^2-p^2k'^2}+(p^2-n^2)$ is equal to $\frac{3}{4}\beta A^2$ and p^2-n^2 is negative. So p^2-n^2 cannot be arithmetically greater than $\sqrt{\alpha^2-p^2k'^2}$. This sets an upper limit to the value of excess tension.

(7) This upper limit being $\sqrt{\alpha^2-p^2k'^2}$ increases with increase in the value of α.

If the frictional term involving the square of the velocity be omitted, *i. e.* if k be zero, the amplitude graph will become a strict parabola. There will be no upper limit to the value of the amplitude, and therefore the collapse of maintenance will not be explained. If the frictional term involving the first power of the velocity be omitted, *i. e.* if k' be zero, there will be no explanation for the fact that there is a lower limit to the value of α below which there is no maintenance. Facts (5) and (7) will be left unexplained. With the two frictional terms all the facts are indicated.

University College, Rangoon.
May 10, 1921.

LVIII. *On a New Optical Property of Biaxial Crystals. By* C. V. Raman, *M.A., Palit Professor of Physics in the Calcutta University, and* V. S. Tamma, *M.Sc., Lecturer in Physics, Meerut College, India* *.

1. *Introduction.*

A FACT of singular interest and importance in the optics of crystalline media which appears hitherto to have been overlooked is that a plate of a biaxial crystal bounded by parallel faces is capable of focussing divergent rays proceeding from a distant light-source and forming *real* images of it. Very simple apparatus will suffice to observe this phenomenon. The incandescent filament of a tiny 2-volt lamp or an illuminated pin-hole serves as a suitable source of light. At some distance from it is placed a crystal of aragonite cut and polished with parallel faces at right angles to the bisectrix of the acute angle between the optic axes. On suitably orienting the crystal and examining the pencil of light which has passed through it, a real erect unpolarized image of the luminous filament may easily be picked up and traced continuously away from the crystal for a considerable distance. There is no difficulty in receiving and observing the image directly on a plate of ground glass if desired.

The image is sharp and bright and practically achromatic if the object and the place of observation are both within a few centimetres of the crystal, one on each side. As either the object or the place of observation is drawn away from the crystal the image spreads out into a spectrum. Using monochromatic light, however, it can be seen that the image remains quite well defined and sufficiently bright to be

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* Communicated by Prof. A. W. Porter, F.R.S.

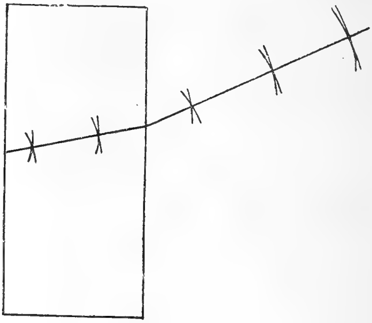
traced for a distance of some 30 or 40 cm. from the crystal. The effects are specially beautiful if observed in the light of a mercury vapour lamp. Separate images of the pinhole corresponding to the yellow, green, and violet radiations of the mercury vapour may be seen, and images corresponding to the fainter components of the line spectrum may also be observed by cutting out the superfluous light with suitable colour filters. A simple slit with a plate of aragonite crystal and an eye-lens to observe the image thus functions as a little spectroscope, which has quite a marked dispersion in the region of shorter wave-lengths.

It should be remarked that these optical images formed by an aragonite plate differ from those formed by an ordinary converging lens in several respects. The images in the present case are *real*, *erect*, and of *unit magnification* irrespective of the distance of either object or image from the crystal. Further, the image is *continuous*, that is, it may be observed anywhere in the prolongation of a certain line for a considerable distance from the crystal and not merely at a single point as in the case of the images formed by a lens. Also the images appear sharply defined in a field of diffuse light, showing that only part of the energy passing through the crystal is brought to a focus. The object being fixed, the image moves when the orientation of the crystal is altered, but not when the plate is moved in its own plane. The focussing property, in other words, appears to be related to a fixed direction within the crystal. In order that the image may be within the field of observation it is necessary, in fact, that the bundle of light-rays should pass through the crystal roughly in this fixed direction, which appears to be that of either axis of single ray velocity in the crystal.

2. *Explanation of the Phenomenon.*

The fact last mentioned suggests a mode of approach to a theoretical explanation of the phenomenon. As already mentioned, the object may be placed at a distance from the crystal, but for simplicity we shall first consider the case in which the object is a point source of light placed just on one of its surfaces. The form of the wave-fronts in the disturbance diverging within the crystal is the Fresnel surface of two sheets which, as is well known, has a singular point in the direction of either axis of single-ray velocity. If we resolve the wave-front into the group of plane waves of which it is the envelope, we see at once that the singularity is really the crossing point of an infinite number of plane waves the normals to which generate the surface of a cone, and hence the intensity of the disturbance at the singular point must be very great in comparison with that at other points on the wave. On emergence from the crystal the singularity persists, and, since in its immediate neighbourhood the wave-front is approximately symmetrical in shape about the axis of the cone of normals, it can easily be seen that the advancing front would retain the same general configuration exhibiting a singularity or concentration of luminosity along its course, as indicated in fig. 1.

Fig. 1.



We have thus in effect a continuous image of the source along a line. When the source instead of being placed on the surface is removed to a distance from the crystal, the waves which diverge from it are in the first instance spherical, but on entry into the crystal these divide at once into two sheets, the points of intersections of which must be in the nature of foci or concentrations of luminosity in the wave-front. On emergence of the waves from the crystal the same effect is propagated outwards, giving a continuous focus or image of the source in much the same way as in the case illustrated in fig. 1. When the luminous source is of finite dimensions we have an image corresponding to each point of it, and it is easy to see that we should have a complete picture built up which would be of the same dimensions as the source and similarly oriented.

The spectral dispersion of the image is also easily understood. For, the direction in which the singularity travels within the crystal being inclined to the normal to the plate, the direction in which the singularity travels on emergence from the crystal depends on the refractive index and hence must make a greater angle with the normal to the plate for the shorter wave-lengths. This is exactly what is actually observed. In an exact quantitative discussion the fact that the direction of the axis of single-ray velocity in the crystal varies with the wave-length must also be taken into account. A fuller discussion of this point and of the resolving power of the crystalline plate regarded as a spectroscope in itself would be of interest. This would obviously require a determination of the distribution of luminosity in and around the point of singularity in the wave-front. It is hoped at an early opportunity to carry out a detailed investigation on these points.

3. *Summary and Conclusion.*

(*a*) The paper describes a new optical effect observed with a biaxial crystalline plate, viz., that such a plate though bounded by parallel faces, is capable of forming on one side of it when suitably oriented a *real* erect image of a source of light such as a luminous filament placed at some distance from it on the other side.

(*b*) The characteristics of this image-forming property are set out in detail, a noteworthy feature being the spectral resolution of the image which occurs when either the object or the image is at a considerable distance from the crystal.

(*c*) A theoretical explanation of the phenomenon is suggested, viz., that the singular point in the Fresnel wave-surface is a locus of maximum intensity, and, owing to the fact that the wave-form on emergence from the crystal retains its general character, we get a continuous concentration of luminosity along a line any point of which is in effect an optical image of the source.

The investigation described in this paper was carried out in part in the senior author's laboratory at Calcutta, and in part at University College, London, during the visit to England of the senior author, who wishes to express his cordial thanks to Prof. A. W. Porter, F.R.S., for his hospitality and kind interest in providing the necessary facilities for the work.

LIX. *Some Problems of the Mass-Spectrograph.*

By F. W. Aston, *D.Sc., F.R.S., and* R. H. Fowler, *M.A.*[*]

§ 1. *Introduction.*

IN the account of the principle of the Mass-spectrograph which appeared in this journal[†], and in subsequent papers describing the constructional details and the results obtained by its means[‡], attention was called to certain points, *e.g.* the linearity of the mass-scale and the possibility of improved focussing, which at that time had not been fully investigated. The following paper contains a mathematical analysis of these points and suggests the directions in which development is most likely to take place. It also supplies an answer to a criticism recently expressed as to the efficacy of the apparatus for the analysis of positive rays.

§ 2. *The distribution of the mass-spectrum over the photographic plate.*

An inspection of actual photographs shows that the various lines of the mass-spectrum are distributed along the plate in such a way that the distance of any image from the fiducial spot is very nearly a linear function of the mass m. It was suggested[§] that the unexpected linearity might be due to some special feature in the geometry of the apparatus. We have now worked out the distribution exactly, and can account for the linear mass-scale. We can also show that the actual observed positions of the lines agree closely over the whole scale with the positions calculated on simple assumptions. This is satisfactory in that it shows that the paths are not seriously distorted by stray fields.

In fig. 1, let O be the centre of the magnetic field, assumed uniform and circular, of radius d. Let Z be the virtual focus from which the rays diverge after passing the electric field, and F their focus on the plate which lies along ZF. Let R be the radius of the circular path (centre C) of rays of mass m in the magnetic field, and let p be the length of ON, the perpendicular from O on ZF. The angle ϕ is the angle at C and $F\hat{Z}O=2\theta$. The angles θ and ϕ are the angles through which the rays are bent by the electric and

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[*] Communicated by the Authors.

[†] Phil. Mag. ser. 6, vol. xxxviii. p. 707 (1919).

[‡] *Ibid.* vol. xxxix. pp. 449, 611; vol. xl. p. 628; vol. xlii. pp. 140, 436.

[§] *Ibid.* vol. xxxix. p. 454.

magnetic fields respectively. Then

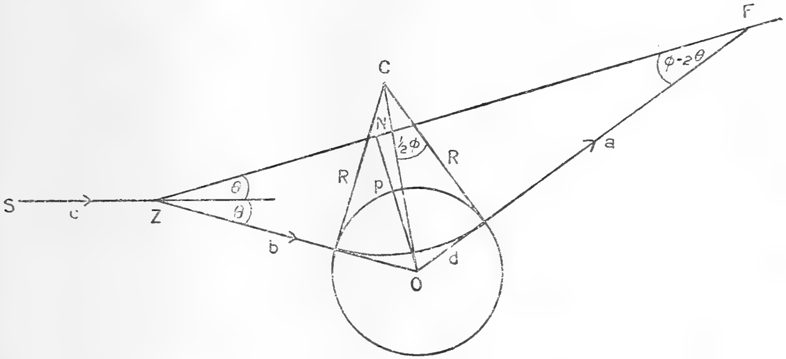
$$\tan \tfrac{1}{2}\phi = d/\mathrm{R},$$

and we know that, as the energy is constant, R varies as $\sqrt{m}$. We may therefore write

$$\tan \tfrac{1}{2}\phi = \sqrt{(m_0/m)}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where m_0 (a constant) can be interpreted as that mass which under the conditions of the experiment is bent through one right angle in the magnetic field. Equation (1) expresses in an exact and convenient form the same facts as equations (1) and (2) of the first paper already cited. It is only through m_0 that the actual values of the fields affect the mass-scale on the plate.

Fig. 1.



It appears from fig. 1 that

$$\mathrm{NF} = p \cot(\phi - 2\theta) = p\,\frac{1 + \tan\phi \tan 2\theta}{\tan\phi - \tan 2\theta}.$$

But $$\tan\phi = \frac{2\tan\frac{1}{2}\phi}{1 - \tan^2\frac{1}{2}\phi} = \frac{2\sqrt{(mm_0)}}{m - m_0}$$

by (1). Hence

$$\frac{\mathrm{NF}}{p} = \frac{m - m_0 - 2\sqrt{(mm_0)}\tan 2\theta}{2\sqrt{(mm_0)} - (m - m_0)\tan 2\theta} \quad . \quad . \quad . \quad . \quad (2)$$

N is of course a fixed point, which in the actual apparatus is approximately 5·4 cm. behind the fiducial spot. When m_0 and the geometrical constants p and θ are known, equation (2) enables us to calculate the position of the image on the plate for any desired mass.

§ 3. *The linearity of the mass-scale.*

It was observed that in the most important part of the plate the mass-scale was nearly linear—more precisely that NF was proportional to m over a wide range. Equation (2) enables us to explain this, and in fact to prove that *such linearity must always occur near* $\phi=4\theta$, which agrees exactly with experience. For if we write $(m/m_0)^{\frac{1}{2}}=z$, we have

$$\frac{\mathrm{NF}/p}{m/m_0}=\frac{z^2-1+2z\tan 2\theta}{z^2\{2z-(z^2-1)\tan 2\theta\}}.$$

An approximately linear scale of the observed nature will occur where

$$\frac{d}{dm}\left(\frac{\mathrm{NF}/p}{m/m_0}\right)=0, \quad i.e.\ \frac{d}{dz}\left(\frac{\mathrm{NF}/p}{m/m_0}\right)=0.$$

On differentiation and simplification we find that

$$\frac{d}{dz}\left(\frac{\mathrm{NF}/p}{m/m_0}\right)=\frac{2(z\tan 2\theta-1)\{(3z^2-1)\tan 2\theta+z(z^2-3)\}}{z^3\{2z-(z^2-1)\tan 2\theta\}^2},$$

which vanishes when $1/z=\tan 2\theta$, *i.e.* when

$$\tan\tfrac{1}{2}\phi=\tan 2\theta.$$

Thus the mass-scale will be approximately linear near $\phi=4\theta$.

Actual numerical calculation by (2) shows that the approximation to linearity should be (as was observed) very close. For the actual apparatus $\theta=\frac{1}{12}$ radian, $\tan 2\theta=0{\cdot}168$. Values of $\frac{\mathrm{NF}/p}{m/m_0}$ in arbitrary units are given in the following table :—

m/m_0.	$\frac{\mathrm{NF}/p}{m/m_0}$.	m/m_0.	$\frac{\mathrm{NF}/p}{m/m_0}$.
44	139	32	138
42	138	30	138
40	138	28	139
38	137	26	140
36	137	24	141
34	137	22	143

The value of m/m_0 corresponding to $\phi=4\theta$ is given by

$$m_0/m=\tan^2\tfrac{1}{2}\phi=\tan^2 2\theta=0{\cdot}0272,$$

$$m/m_0=36{\cdot}7.$$

§ 4. *Practical use of the mass-scale.*

Let us denote the distance of an observed image from the fiducial spot by D. Then D and NF differ by some constant k—about 5·4 cm. in the existing spectrograph. Equation (2) shows that in all cases the relation between D and m has the form

$$D = f(m/m_0). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where f is a function in which all the coefficients, p, k, and $\tan 2\theta$ are geometrical constants; the fields affect m_0 and m_0 alone. In the actual apparatus, which was not quite rigid, p, k, and 2θ probably altered slightly each time the apparatus was assembled, but otherwise were strictly constant.

The only assumption made in the actual analysis of the plates was the following:—*If* D_1 *and* D_2 *are the distances from the fiducial spot of any two points on the plate and* m_1 *and* m_2 *the corresponding masses, for given values of* D_1 *and* D_2 *the ratio* m_1/m_2 *will be the same in every photograph taken with the same setting up of the apparatus.* This is a direct consequence of (3). For so long as the apparatus be not subjected to a new set of stresses, the function f will remain unaltered. In any one photograph we have

$$D_1 = f(m_1/m_0), \qquad D_2 = f(m_2/m_0),$$

and in any other (with different fields)

$$D_1 = f(m_1'/m_0'), \qquad D_2 = f(m_2'/m_0').$$

But if $m_0' = \alpha m_0$ it follows at once that we must have $m_1' = \alpha m_1$, $m_2' = \alpha m_2$, and therefore in all cases

$$m_1'/m_2' = m_1/m_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which is the hypothesis mentioned. The argument is more general than equation (2), as an equation of the form (3) must hold even when actual fields are considered instead of the idealized fields of § 2. The practical accuracy of the theoretical relations (3) and (4) was amply verified by the fact that the construction of a consistent calibration curve—that is, the evaluation of the function f—was possible for all photographs taken with one setting up of the apparatus. Owing to the fact that f is very nearly linear, the calibration curve results in applying only a small correction to the observed D to make it proportional to m. The certainty of the results is therefore greatly increased.

§ 5. *A comparison of the calculated mass-scale with an actual photograph.*

The existing spectrograph was designed so that $k=5{\cdot}4$ cm. approximately and $\tan 2\theta=0{\cdot}168$. The values actually realized may be slightly different. The designed value of p is less certain, but is about $2{\cdot}3$ cms. In order to compare a calculated and observed mass-scale we have assumed the above values for k and $\tan 2\theta$. Equation (2) now takes the form

$$\frac{D+5{\cdot}4}{p}=f(m/m_0),$$

where the function f is exactly known. We do not know m_0 directly or the exact value of p, and therefore m_0 and p may be regarded as disposable constants. In order to determine them, values of $\log_{10}(D+5{\cdot}4)$ were tabulated for observed values of D, for which the values of m are known, and also values of $\log_{10} f(m/m_0)$ for selected values of m/m_0. The difference of these logarithms, $\log_{10} p$, should be constant and m_0 must and can be selected so as to obtain this constancy. In the photograph analysed it happens that, thus determined, $m_0=1$. The corresponding value of p was $2{\cdot}388$, in agreement with the designed value.

Assuming the values of m_0 and p, and the above values of k and $\tan 2\theta$, values of D were calculated for a series of values of m, and are shown by the continuous curve of fig. 2. Observed values of D for the actual lines on the plate are shown by circles. The agreement is excellent, in view of the fact that the assumed values of k and $\tan 2\theta$ are not reliable to the required degree of exactness.

§ 6. *A discussion of some recent criticisms.*

In this connexion some recent criticisms by Sir J. J. Thomson[*] call for comment. He there discusses the focussing effect of the electric and magnetic fields deflecting in opposite directions, and assumes an ideal arrangement practically identical with the existing instrument. He points out that the emergent rays for each value of e/m must have a caustic, but that when (as here) rays of constant kinetic energy are selected only certain portions of the caustic will be touched by the existing rays, and the photographic plate must be placed so that it passes through the

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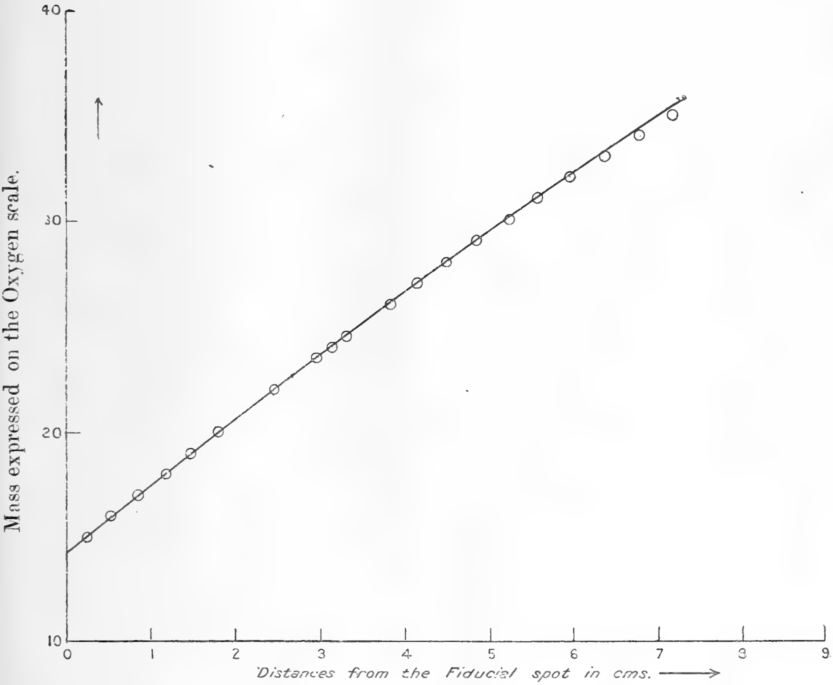
[*] Proc. Roy. Soc. A, vol. xcix. p. 93 (1921).

existing element of each caustic. He gives an equation (p. 94) for the position of the plate.

This position had been already established by another argument in the first paper cited, so that to this order of accuracy Thomson's discussion agrees with ours.

He then goes on to give a formula for the distance of the image along the plate as a function of e/m, and points out that this distance will not be a linear function of the mass.

Fig. 2.



The order of approximation, however, which he uses is, we think, inadequate for the purpose ; the full analysis given in the preceding sections is needed to obtain that true relation. We have there seen that the observed distributions are a good fit with the theory, and that the deviations from a linear relation are very small. Such deviations as occur are simply allowed for by the use of a calibration curve in reducing the observations, so that criticism of the results based on this non-linearity cannot be regarded as of great weight.

§ 7. *The resolving power.*

Equation (2) enables us to discuss accurately the resolving power of the apparatus, but we begin with some preliminary considerations. In fig. 1 we denote ZO and OF by b and a respectively, and the centre of the slit system by S, where $SZ=c$. We consider the spread of an otherwise homogeneous beam of rays which pass through the slits at slightly different angles distributed over a range $\delta\alpha$. This spread arises of course from the width w of the slits and we have

$$\delta\alpha=2w/T, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where T is the distance between them. The beam may be taken as diverging from S. We are not here concerned with the focussing for different velocities, which may be assumed perfect.

The total path of the rays is of length $SZ+ZO+OF$ or $a+b+c$ very nearly, and therefore the linear spread of the beam at F is $(a+b+c)\delta\alpha$ at right angles to OF. This can be converted when desired into an expression for the width of the image on the plate. At the moment we regard it as equivalent to a spread in ϕ equal to $(a+b+c)\delta\alpha/a$.

Now the instrument will resolve beams of different masses if the change in ϕ for change of mass is greater than the geometrical spread, and the greater ϕ for a given mass and given spread the greater the resolving power. Thus we may take

$$\frac{\phi a}{(a+b+c)\delta\alpha}$$

as a rough measure of the resolving power of the instrument.

Now the relation between a and b is (*loc. cit.*)

$$b/a=(\phi-2\theta)/2\theta,$$

and we find on eliminating the variable a that the resolving power is measured by

$$\frac{\phi}{\delta\alpha\left\{\frac{\phi}{2\theta}+\frac{c}{b}\left(\frac{\phi}{2\theta}-1\right)\right\}} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It is our object to make (6) as large as possible. To do this we can keep $\delta\alpha$ and c/b as small as possible, but there are strict limits to what can be done in this direction. The only other method is to increase ϕ without increasing the denominator, which can only be done by making ϕ and θ both large together. It is important to note that larger resolving power can only be obtained by increase of ϕ if θ is increased as well.

These arguments are too rough to give an exact value for the resolving power of the actual apparatus. This we can obtain by considering linear displacements along the plate. The width of the image on the plate is

$$(a+b+c)\delta\alpha \operatorname{cosec}(\phi-2\theta).$$

Consider the region near $\phi=4\theta$, $a=b$ in the actual apparatus, where $a+b+c=26$ cm. and $\mathrm{T}=10$ cm. Thus $\delta\alpha=w/5$ and the width of the image (in cm.) is $31{\cdot}4w$.

By direct calculation with formula (2), with $p=2{\cdot}388$ cm., we find that there is an interval of 0·797 cm. between the corresponding parts of the images for $m/m_0=34$, 36. This corresponds to an interval of 0·139 cm. for a change of 1 per cent. in m. The actual width of the slits used was about 1/25 mm., so that the theoretical width of the image in this region is 0·126 cm. This agrees very well with the actual image widths, showing that there was little (if any) increase in width due to inexact focussing, and further that theoretically the apparatus should be able to resolve lines corresponding to masses differing by just less than 1 per cent. In actual practice a slightly greater resolving power was obtained, probably by using the ends of the images which correspond to a narrower part of the slits.

These considerations show that the theory and practice of this form of mass-spectrograph are in very satisfactory agreement, and present no anomalous and disturbing discordances.

§ 8. *Possible improvements in focussing and in the position of the photographic plate.*

The focussing achieved by the existing apparatus is only "first order focussing"; it is not exact, but the rays all touch a caustic and the plate is placed to pass through the points of contact of the rays actually existing. As a result, many of the rays must have a very oblique impact on the plate, which is unsatisfactory for a variety of reasons and should be avoided if possible. It is natural therefore to try so to modify the apparatus that both the focussing and the position of the plate may be improved. The only feature which is really at our disposal is the *shape* of the magnetic field. It ought to be possible so to modify the shape that either or both of the objects might be achieved. It turns out that it is unlikely that any serious improvement is feasible in the position of the plate, but that improvements should be possible in the focussing. The arguments by which one can obtain these results are as follows.

Consider, first, the problem of trying to achieve focussing at a (roughly) constant distance from the centre of the magnetic field. The equations governing the deflexions are (*loc. cit.*)

$$v^2\theta = \text{const.}, \qquad v\phi/\mathrm{L} = \text{const.},$$

where L is the length of the path in the magnetic field and is now no longer assumed constant. On differentiating we have

$$\frac{d\theta}{\theta} + 2\frac{dv}{v} = 0, \qquad \frac{d\phi}{\phi} + \frac{dv}{v} = \frac{d\mathrm{L}}{\mathrm{L}},$$

and on eliminating v,

$$\frac{2d\phi}{\phi} - \frac{d\theta}{\theta} = \frac{2d\mathrm{L}}{\mathrm{L}}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We shall, for example, achieve focussing at a constant distance a from the magnetic field (fig. 1) if we make $d\phi = 2d\theta$ for all values of ϕ by proper adjustment of $d\mathrm{L}$. That is to say, we must have by (7),

$$\frac{d\phi}{\phi} - \frac{d\phi}{4\theta_0} = \frac{d\mathrm{L}}{\mathrm{L}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

for θ is a constant θ_0 the same for all rays. Equation (8) can be integrated and we find that, putting $\phi_0 = 4\theta_0$,

$$\mathrm{L} = \frac{\mathrm{L}_0\phi}{\phi_0} e^{-\frac{\varphi - \varphi_0}{\varphi_0}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This gives the necessary length of path L as a function of ϕ, and thus determines the shape of the *trailing edge* of the magnetic field. It is clear that it is the shape of the trailing edge only which is relevant here, for the rays for various values of m all enter at the same point on the leading edge.

So far all is satisfactory, but the result will only be of practical value if the curvature of the trailing edge is not too large compared with the size of the field. If the edge is very sharply curved, the stray field will be large and may be expected to spoil the effect which we desire to produce. The calculation of this radius of curvature ρ is straightforward.

If we take as axes of coordinates the tangent and normal to the rays at their point of entry into the magnetic field, the coordinates of their point of emergence may be shown to be

$$x=\frac{\mathrm{L}\sin\phi}{\phi},\qquad y=\frac{\mathrm{L}(1-\cos\phi)}{\phi},$$

and therefore by (9)

$$x=\frac{\mathrm{L}_0}{\phi_0}\sin\phi\, e^{-\frac{\phi-\phi_0}{\varphi}},\qquad y=\frac{\mathrm{L}_0}{\phi_0}(1-\cos\phi)e^{-\frac{\phi-\phi_0}{\phi_0}}.$$

The values of ρ can now be determined for general values of ϕ by the usual formula. The expression is complicated and for our purpose it is sufficient to consider $\phi=\phi_0$ and assume that ϕ_0 is moderately small. The leading term in the expression for ρ is then

$$-\tfrac{1}{4}\mathrm{L}_0\phi_0{}^2.$$

The minus sign denotes that the concave side of the trailing edge is outwards. In the existing instrument $\phi_0=4\theta_0=\frac{1}{3}$. To achieve the desired result we should require a concave trailing edge in this neighbourhood of radius $\frac{1}{36}\mathrm{L}_0$, where L_0 may be taken to be the diameter of the magnetic field. This is far too severe to be of practical use. For $\phi_0=4\theta_0=\frac{2}{3}$, the radius of curvature would have to be $\frac{1}{9}\mathrm{L}_0$, which is perhaps just practicable if L_0 is large. Thus a serious improvement in the position of the plate is barely feasible.

§ 9. *Second order focussing.*

In order to obtain the conditions for more exact focussing we must start by examining the form of the beam for given m after deflexion in the electric field. It is easily shown that, when the electric field is a uniform field of intensity X acting over a length l, the rays of various velocities all diverge *exactly* from a virtual focus Z at the centre of the field on the line of entry. For the path of the particle, charge e, mass m, in the assumed field is a parabola, whose equations referred to axes Oxy are (fig. 3) :

$$x=v\cos\alpha\, t,\qquad y=v\sin\alpha\, t-\tfrac{1}{2}\mathrm{X}et^2,$$

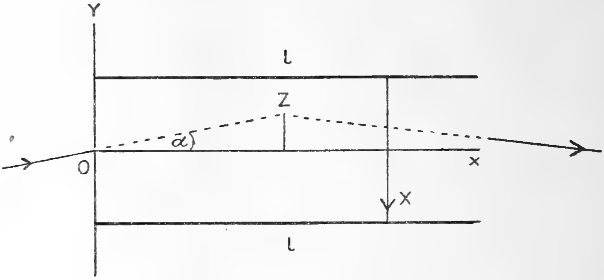
$$y=x\tan\alpha-\frac{\mathrm{X}e}{2v^2}\sec^2\alpha\, x^2.$$

The emergent ray starts from the point

$$\left(l,\ l\tan\alpha-\frac{Xel^2}{2v^2}\sec^2\alpha\right).$$

at the slope $$\tan\alpha-\frac{Xel}{v^2}\sec^2\alpha.$$

Fig. 3.



Its equation can therefore be put in the form

$$y-l\tan\alpha+\frac{Xel^2\sec^2\alpha}{2v^2}=\left(\tan\alpha-\frac{Xel\sec^2\alpha}{v^2}\right)(x-l),$$

or $$y-x\tan\alpha=-\frac{Xel\sec^2\alpha}{v^2}(x-\tfrac{1}{2}l), \quad . \quad . \quad . \quad (10)$$

which passes through the point $(\frac{1}{2}l, \frac{1}{2}l\tan\alpha)$,, *i. e.* Z, for all values of v.

To find the conditions for more accurate focussing after passing the magnetic field we may therefore think of the rays incident on the magnetic field as diverging exactly from a point distant b' from its leading edge, where b' is less than the b of fig. 1 by d, or $\frac{1}{2}$L, the radius of the field. We shall assume, to simplify the discussion, that the leading edge is plane and at right angles to the median ray, which is deflected through an angle θ_0 in the electric field.

The path of a typical ray is shown in fig. 4, in which A is the point of entry and B the point of emergence. After reduction the exact equation of the emergent ray, referred to axes Oxy, can be put in the form

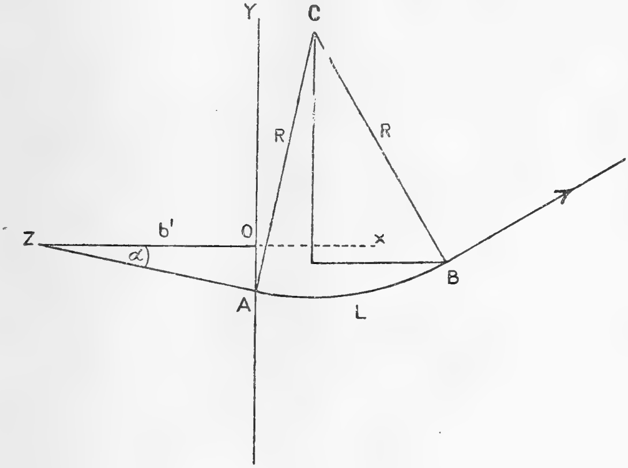
$$y\cos(\phi-\alpha)-x\sin(\phi-\alpha)+Bv(1-\cos\phi)$$
$$+b'\tan\alpha\cos(\phi-\alpha)=0, \quad . \quad (11)$$

where B is the constant $L/(v\phi)$ and α and v are related by the equation, valid when θ_0 is small, for the electric deflexion

$$(\theta_0+\alpha)v^2=\text{const.}$$

The focus of the emergent beam is the point where the line (11) touches its caustic (*i.e.* the envelope of the family (11) when the parameter α is varied). This point can be determined (by the usual rule) by differentiating with respect to α, and determining $d\phi/d\alpha$ and $dv/d\alpha$ from the deflexion equations. This leads to a position of the focus agreeing when ϕ is small with the position already determined (*loc. cit.*) by simpler arguments. In order to obtain second-order focussing the coordinates of this point on the caustic must also satisfy the equation obtained by differentiating (11) *twice* with respect to α.

Fig. 4.



The exact condition thus obtained is an equation for $d^2\text{L}/d\alpha^2$ and is somewhat complicated. In order to appreciate its meaning, we shall assume that $d\text{L}/d\alpha=0$ and retain only the lowest powers of ϕ. It then reduces to the relation

$$\frac{\text{L}''}{\text{L}}=\frac{1}{4\theta_0^2}\cdot\frac{b'+\frac{1}{2}\text{L}}{b'+\text{L}(1-\phi/4\theta_0)}.$$

Near $\phi=4\theta_0$, the important neighbourhood, and for $\theta_0=\frac{1}{12}$ we have L''/L somewhat greater than 36—for $\theta_0=\frac{1}{6}$ somewhat greater than 9. If we work out the radius of curvature ρ of the trailing edge of the field we find, with $d\text{L}/d\alpha=0$

and retaining only the lowest powers of ϕ,

$$\rho = -\frac{\{b' + \mathrm{L}(1-\phi/4\theta_0)\}^2}{\mathrm{L}''},$$

$$= -\frac{4\theta_0^2\{b' + \mathrm{L}(1-\phi/4\theta_0\}^3}{\mathrm{L}(b'+\frac{1}{2}\mathrm{L})}.$$

We observe that this radius of curvature can be kept reasonably large by making b' fairly large compared with L. For example, if $b'=2\mathrm{L}$, $\phi=4\theta_0$, the radius required is $\frac{64}{5}\theta_0^2\mathrm{L}$. Even when $\theta_0=\frac{1}{12}$, as in the present apparatus, this is $\frac{4}{45}\mathrm{L}$, and if $\theta_0=\frac{1}{6}$ it is $\frac{16}{45}\mathrm{L}$, which is by no means unmanageably small. It is therefore possible that the focussing can be improved by this means, although it is not so likely to be possible to improve the position of the plate. The reason why this improvement is possible without the use of an unreasonably small radius of curvature on the trailing edge of the field is that, by making b' large, we can scatter the rays of different velocity well before they impinge on the leading edge of the field. Thus the necessary difference of path length can be achieved on paths which are not too close together—that is, by a trailing edge of reasonable curvature.

In actual practice the curvature would be applied to the leading edge, since this arrangement possesses all the advantages, from a structural point of view. In the region of $\phi=4\theta_0$, where the paths are symmetrical about the magnetic field, it is theoretically immaterial to which edge the curvature is applied.

§ 10. *Considerations of the dimensions of the apparatus.*

In designing physical instruments of precision, it is of importance to study the absolute scale of dimensions likely to yield the best results. Now, pressures being equal, the shorter the path of the beam of positive rays between the cathode and the photographic plate the less likely it is to lose intensity and sharp outline through collisions. Also the smaller the area of the plate affected by a beam of given intensity the easier will be its detection and the more accurate its measurement, for we are very far at present from the limits of accuracy of the measurement of position on the plate determined by the fineness of the grain of the emulsion. Hence both these considerations point to an instrument of the smallest practicable dimensions.

The electric field offers no restrictions to such a development, for, once having decided the value of the deflexion θ_0 and the potential at our disposal to produce it, the only quantity fixed is the *ratio* of the length of the plates to their distance apart. Their absolute dimensions are only limited by considerations of convenience of construction.

The magnetic field, on the other hand, unfortunately dictates an inferior practical limit to the size of the instrument in an unequivocal manner. We have from the original exact equation for the motion of the charged particle in the magnetic field of intensity H,

$$\frac{\mathrm{HL}}{\phi}=\frac{mv}{e}=\left(2\frac{m}{e}\mathrm{V}\right)^{\frac{1}{2}},$$

where V is the potential through which the particle has fallen in the discharge tube. If we express V in volts and m on the ordinary chemical scale (O=16) we get approximately

$$\mathrm{HL}/\phi=144(m\mathrm{V})^{\frac{1}{2}}.$$

Now H cannot very well be greater than 17,000 gauss for large pole-pieces. Actually the highest value used so far in this work is 15,000 gauss. Taking the values of the existing apparatus $\phi=\frac{1}{3}$ radian and H=15,000, and allowing V to range from 20,000 to 50,000 volts, we find that while for the hydrogen atom ($m=1$) the length of the field required ranges from 0·45 to 1·0 cm., for mercury ($m=200$) it must range from 6·4 to 14·1 cm. (The actual length is 8 cm.)

We see therefore that while it is possible to design a mass-spectrograph of precision on a small scale to investigate elements of the lightness of hydrogen or helium, an apparatus capable of resolving the isotopes of the heavy elements must of necessity be on a considerable scale. Increase in the scale of the apparatus brings the necessity for extremely low pressure and other technical difficulties in its train, so that it appears probable that really great increase in resolving power, as in the case of X-rays, will have to come ultimately from increase in the intensity of the beam of rays, enabling extremely narrow slits to be employed.

Summary.

Some points raised by the performance and further design of the mass-spectrograph are discussed.

The linearity of the mass-scale and the resolving power of

the existing apparatus are explained. The agreement between theory and experiment is shown to be good.

The questions of improvement in position of the plate and second-order focussing are discussed. The latter is shown to be feasible.

Lines on which future improvements are possible are suggested.

Trinity College, Cambridge.
November 1921.

LX. *A Definition of Simultaneity and the Æther.*

By E. H. Synge*.

I PROPOSE to show that a definition of absolute simultaneity is involved in the generalized coordinate frames assumed in relativity.

Considering two events E, E′, located at the points P, P′, in an arbitrary frame F, and joining P, P′ by any line L in F, we may assign, in an infinite number of ways, another frame F′, which, at every instant, at every point of L, has a finite component of relative velocity normal to L. The points of L trace out a surface S in F′, and if Q be the point in S occupied by P at a specific instant, and if M be any line in S passing through Q, then the point R in L, at which M and L instantaneously intersect as L crosses M, will move along L as L moves in S, and in the immediate neighbourhood of P this motion of R along L will, according to the direction of M in S at Q, be either inwards to, or outwards from, P. The possible directions of M at Q are divisible into two groups, corresponding to these two different senses of the motion of R, and it is clear, on grounds of continuity, that the two groups in question are separated by a limiting direction of discontinuity, for which the motion of R along L at P, and obviously also of R along M at Q, would be indeterminate in sense, and of infinite velocity.

We shall define this limiting direction as instantaneously codirectional with L at P, and, considering the entire length of L, it appears without difficulty, in the supposed circumstances of motion, that through each position instantaneously occupied by P in S, a single line in S can be drawn, which at all points of its length is instantaneously codirectional with L as the latter crosses it. For, supposing, on the contrary, that two such lines passed through a point Q′ in S, and

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* Communicated by the Author.

considering a small triangle in S, whose sides are formed by two lines M′, M″, which pass through Q′, diverging slightly from the supposed two lines of instantaneous codirectionality, and whose base is the track of a specific point P″ of L, we see that the point R′ of intersection of L, first with M′, and then with M″, travels along L to Q′, and then along L in the reverse direction to meet the point P″. But, by taking the lines M′, M″, sufficiently near to the critical directions the velocity of R′ can be increased beyond any assigned limit, while that of P″ travelling through S remains finite. We should therefore have two points proceeding over finite distances, the one at a finite, the other at an infinite velocity, and reaching the same point together, a thing which no question of time units can render conceivable. It will be noticed that the velocity of R along L is in no respect limited by, or in any way dependent on, or connected with, the velocity of light, which does not enter into the question at all.

Some additional considerations are perhaps called for here as being necessary to justify the attribution of a definite sense of motion along L to the phase point R, where the velocity exceeds that of light. For this purpose we may for simplicity suppose that the surface S is the plane of the paper, and conceive an apparatus in which two very fine split needles N_1 and N_2 are pivoted about points O_1 and O_2, O_1 and O_2 being out of and above the surface S, and situated near the tangent to M through Q, and on opposite sides of M with respect to Q, where Q is no longer taken as the terminal point of M. N_1 and N_2 are free to move in such a way that each always touches M at a point, and they are set initially with their extremities passing through S, very close to Q, the needles making very small angles with M where they touch the latter, and each touching M at the same side of Q as its own pivoting point.

N_1 and N_2 are now caused to move so that, as L slides over S, the point where each touches M continually coincides with R. In this motion of L one needle will be struck by L on the lower edge and raised, while the other needle will be struck on the upper edge and depressed, and the direction of motion of R along L can be defined according to the particular needle which is struck on its upper edge. In this apparatus O_1 and O_2 can, except for the limiting direction, always be chosen so near to the tangent to M at Q, that no portion of the needles need have a velocity as great as light, although the velocity of R at P may be many times greater than this. It is obvious that we are justified in speaking quantitatively of the velocity of the phase point R along L, precisely as if we were speaking of a material point or light wave, while the argument employed to demonstrate the uniqueness of the line of instantaneous co-directionality becomes quite definite when considered in connexion with such apparatus.

We shall call the system of these lines of instantaneous codirectionality, corresponding to the different positions occupied in S by P, the system (LF′) and we shall define the events E and E′ as simultaneous if both occur in the transit of L across the same line of (LF′).

To prove that this definition is independent of F, F′, and L, we first infer from the definition of instantaneous codirectionality, that if two lines cross one another, as, for example, L and M, and have at all points of this transit finite normal components of relative velocity, then if they are instantaneously codirectional at any point, the line which is the locus of the events of their transit in any third frame, will, at that point, be codirectional with both lines. Considering the locus in a third frame of the transit of L across a member of (LF′) the definition of simultaneity is seen to be independent of F′, the third frame being interchangeable with F′, where the condition of a finite normal velocity relative to L is observed. It is also obvious that F′ is interchangeable with F, M taking the place of L.

We now join P, P′ by any second line λ in F, and select F′ in such a way that the condition of a finite normal component of relative velocity is satisfied with regard to the closed line $L+\lambda$. There will then, through Q, be a unique closed line $M+\mu$ in F′, which is instantaneously co-directional at all points with $L+\lambda$, as the latter crosses it, and it is clear that the same criterion of simultaneity is satisfied by the passage of $L+\lambda$ across $M+\mu$, as by that of L across M or of λ across μ, L and λ being thus interchangeable and the definition's independence of the particular line L being established. It is clear, further, that if two events are simultaneous with a third, according to this definition, they are also simultaneous with one another, since the line joining their locations in F may be chosen to pass through the third.

The definition is thus absolute, and can be extended throughout the whole universe, while it does not depend in any way upon the Euclidean character of space. The æther also is that privileged frame of space for which, where matter is not in question, light simultaneities coincide with these absolute simultaneities.

The doctrine of relativity, as such, therefore breaks down, and the mathematical transformations it introduces must, if they are valid, be susceptible of an interpretation in terms of these absolute data; while with regard to hyperbolic Space-Time, in which the instantaneous co-directionality of two moving lines is not an absolute property, but dependent on particular frames of reference, it appears that intrinsic contradictions are involved.

Note.—In the above discussion it might have conformed more strictly to the criteria of relativity to have stated that the condition satisfied by F′ is that, in a finite region and time considered, each point of the surface traced out by L in F′ is occupied by one point only of L and for only one instant.

The remark should perhaps also be made that the argument for the indifference of the coordinate frames can be made definite by the introduction of the apparatus described above, in which case we assume, as not open to question, that for great velocities of R the same sense of motion of R along L would be indicated whether O_1, O_2 were fixed in F′ or in F.

LXI. *Remarks on Ionization by Cumulative Action.* By K. T. Compton, *Professor of Physics, Princeton University* [*].

A RECENT, very interesting paper by Professor F. Horton and Miss A. C. Davies [†] brings convincing proof of the importance of radiation in the production of ionization in certain cases in which ionization by direct impact is impossible or improbable. These cases include the formation of arcs in metallic vapours and in helium at voltages less than their minimum ionizing potentials. Experiments now being conducted in this Laboratory by Mr. Duffendack, to test the possibility of the production of similar low voltage arcs in multiatomic gases, have indicated that it is impossible to cause arcs to strike in such gases at any voltages less than their minimum ionizing potentials, even when stimulated by the most intense thermionic currents which can be produced between heavy incandescent tungsten strip electrodes heated by currents through water-cooled leads. Experiments on low voltage arcs in *atomic*

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[*] Communicated by the Author.

[†] Phil. Mag. xli. p. 746 (1921).

hydrogen and *atomic* iodine, produced by dissociation within an incandescent tungsten tube, are now in progress.

The two characteristics of monatomic gases, which probably account for the relative ease of production of low voltage arcs in them, are elasticity of electron impacts and ability of any atom to absorb the resonance radiation from neighbouring atoms. The former characteristic results in the gaining of sufficient energy by every electron to produce either radiation or ionization at an impact, and also in greatly increasing the number of impacts made by an electron in its path between the electrodes. The latter characteristic permits the radiant energy, liberated by each electron impact which results in radiation, to be passed on from atom to atom, and thus multiplies the fraction of atoms which are in the "abnormal" or partially ionized condition. In multiatomic gases the undissociated molecules do not appear to be capable of absorbing the radiation which is produced by electron impacts and which is believed to be characteristic of the dissociated atoms instead of the molecules.

In a previous paper [*] the writer has summarized some evidence that ionization in low voltage arcs cannot be due to effects of single impacts, but must be the cumulative effect of two or more impacts. Additional evidence may be suggested along the following lines.

Consider parallel electrodes distant d apart in a gas at pressure p millimetres and with a difference of potential V, giving an average electric intensity $X=V/d$. Let V_i and V_r be the minimum ionizing and radiating potentials of the gas and let N be the average number of collisions made by an electron per centimetre path. Its mean free path $l=1/N$. If the potential difference V is made equal to or slightly greater than V_i, what is the probability P that an electron may gain a speed sufficient to ionize a normal atom by impact? In a monatomic gas every electron will attain a speed corresponding to V_r despite possible collisions. In passing from the point of potential V_r to that of potential V_i, it is liable to expend its energy in the production of radiation at any impact. If one of these intervening impacts happens to be elastic, the electron is deflected through such an increased path that additional impacts become probable, each with an additional chance for loss of energy by production of radiation. Taking account of this and of the average direction of motion of an electron in the region between V_r and V_i, it is found that the probability of getting through

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[*] Phys. Rev. xv. p. 476 (1920).

this region without loss of energy by radiation is approximately:

$$P=\epsilon^{-\frac{\sqrt{2pN}(V_i-V_r)}{X}},$$

which must at least be of the right order of magnitude. This represents the fraction of the bombarding electrons which attain sufficient speed to ionize a normal atom by a single impact, and is independent of the initial kinetic energy of emission of the electrons from the cathode, provided this does not exceed V_r.

In Table I. are given values of P calculated for various pressures in mercury vapour and helium, assuming the electrodes to be 1 cm. apart. For mercury: $V_i=10{\cdot}4$, $V_r=4{\cdot}9$, $N=75$; for helium: $V_i=25{\cdot}2$, $V_r=20{\cdot}4$, $N=8{\cdot}5$. These gases represent extreme cases of small and large values of P, respectively, under given conditions.

Table I.

p (mm.).	P Hg.	P He.
0·01	0·59	0·98
0·1	$3{\cdot}1\ (10)^{-3}$	0·79
1·0	$7{\cdot}8\ (10)^{-26}$	0·09
3·0	$5{\cdot}0\ (10)^{-76}$	$7{\cdot}3\ (10)^{-6}$
10·0	$9{\cdot}6\ (10)^{-252}$	$2{\cdot}7\ (10)^{-13}$

At the pressures, between 2 mm. and 10 mm., at which the most intense low voltage arcs are obtained, it is evident that any contribution to this ionization due to single impacts against normal atoms is entirely negligible. The same conclusion must be drawn from experimental evidence. In a recent paper * I have shown that the ionization curve in helium shows no discontinuity at the ionizing potential 25·2 volts for pressures exceeding three or four millimetres. Further experiments on arcs in helium † have also indicated that the critical voltage for the helium arc is the minimum radiating potential, near 20·4 volts, rather than the ionizing potential.

It appears, therefore, that while ionization by single

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* Phil. Mag. xl. p. 553 (1920).

† K. T. Compton, E. G. Lilly, & P. S. Olmstead, Phys. Rev. xvi. p. 282 (1920); K. T. Compton & E. G. Lilly, Astrophys. Jour. lii. p. 1 (1920).

impact may be of primary importance in producing ionization in rarified gases, as in Geissler tubes, ionization by cumulative action is of preponderating importance in arcs in monatomic gases and vapours.

As to the nature of this cumulative action, there are four possibilities which have been suggested. The majority of atoms which are in an abnormal or partially ionized state may be in this state either as a result of a previous impact or by absorption of resonance radiation produced by electron impacts against neighbouring atoms. Then the second stage of complete ionization may be brought about, either by an electron impact against the abnormal atom or by its photoelectric ionization by additional radiation.

As the result of a tentative formulation of the theory of ionization by direct successive impacts * and experiments on helium †, the writer came to the conclusion that the actual amount of ionization is much larger than can reasonably be accounted for in this way. It can be shown, for example, that if the observed results are to be explained simply by successive impacts, it would be necessary to take the time constant of damping of resonance radiation to be about a million times greater than any value of this constant which has been found for any substance by direct experiment. Hence, it was concluded that the energy of resonance radiation from neighbouring atoms must contribute to the total energy required for ionization.

If impurities are present in helium, they will be photoelectrically ionized by the helium resonance radiation. Goucher ‡ and others who have obtained experimental evidence of ionization in helium below the ionizing potential have attributed it to such photoelectric ionization of impurities.

Professor Horton and Miss Davies § have criticized the writer's proof of the existence of true ionization of helium below the ionizing potentials as inconclusive on two grounds: (1) the probable photoelectric ionization of neon or other impurity, and (2) uncertainty regarding the significance of a measured ratio R, on whose values the conclusions were based. The following evidence, however, proves these criticisms to be unfounded:—

(1) Although earlier experiments were made with helium, in which a trace of neon was spectroscopically detectable, later experiments in which similar ionization was obtained

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* Phil. Mag. *loc. cit.* † Phil. Mag. *loc. cit.*

‡ Proc. Phys. Soc. xxxiii. p. 13 (1920).

§ *Loc. cit.*

in absolutely pure helium are quoted in the writer's original paper. The degree of purity may be judged by the fact that, in this helium, *arc currents as large as an ampere were obtained at the minimum radiating voltage without observing any spectral line of an impurity.* Every line in the visible line spectrum of helium (excepting the enhanced lines) was observed and, in addition, more than two hundred lines of the band spectrum. It is impossible that such a degree of ionization and such an intense helium spectrum could be attributed to ionization of impurities which were present in too small quantity to be detected in the spectrum.

(2) The criticism of Horton and Miss Davies to the effect that the writer's measurements of R (which is the ratio of the electrometer deflexions observed with the foil and gauze ends, respectively, of a hollow cylinder presented toward the filament) do not give an exact estimate of the proportion of the observed effect due to ionization or radiation separately, is well taken. The uncertainty is pointed out as due to the presence of a photoelectric emission from the sides and back of the cylinder, as well as from its front, due to resonance radiation passed on from atom to atom through the gas. Such photoelectric emission from the sides was neglected in the writer's calculations. Yet the observed variation in R is entirely too large to be accounted for in this way. For instance, at 25 mm. pressure, it would require a photoelectric emission from the sides of the cylinder twelve times larger than that from the foil end to account in this way for the observed value of R. But the area of the sides is only four times that of the face, and they are much less favourably placed as regards the electric field and their accessibility to the radiation. For these reasons the writer stated that the absolute values of R are of little importance, but that the variation of R pointed conclusively to ionization.

For these reasons the writer cannot admit that Professor Horton and Miss Davies have been the first to definitely prove the existence of ionization between the minimum radiating and ionizing voltages in helium, or the essential part played by resonance radiation in producing this ionization. But the work of Horton and Miss Davies strikingly proves that radiation may play an even more important role in cumulative ionization than had previously been suggested, being active not only in maintaining atoms in an abnormal state, but also in photoelectrically ionizing them when in this condition.

It is reasonable to suppose that cumulative ionization becomes an increasingly important factor in ionization as conditions become more favourable to cumulative action and less favourable to direct ionization by single impacts. We should expect, therefore, that cumulative action would be particularly important in the temperature ionization of gases, and therefore that the part played by radiation in promoting temperature ionization would be very important.

An illustration of the possible importance of such a concept of temperature ionization is seen in the opportunity which it affords of explaining certain failures of the exceedingly interesting and important theory of Ionization in the Solar Chromosphere, which has recently been proposed by Dr. Megh Nad Saha [*]. He applies Nernst's equation of the reaction isobar to the calculation of the percentages of ionization of different elements, by considering ionization to be a dissociation with heat of dissociation measured by the ionizing potential, and by assuming the element to be in an enclosure at the temperature T of the Sun's chromosphere. This is equivalent to assuming that the element is subjected to molecular bombardments and black body radiation characteristic of the temperature T. This leads to the conclusion that the degree of ionization of an element at any pressure depends only on its ionization potential and the temperature T. The theory thus developed accounts beautifully for numerous characteristics of the solar spectrum. It has been pointed out by Professor Russell, however, that there are several instances in which Saha's theory seems inadequate [†]. For instance, the ionization potentials of barium and sodium are practically equal, yet barium is apparently completely ionized in the chromosphere, whereas sodium is not, as evidenced by the absence of all except the enhanced lines of barium, which are strong, while the sodium D lines prove an abundance of un-ionized sodium.

This may be accounted for if the influence of radiation in promoting ionization be considered, as will be pointed out in a Note in the Astrophysical Journal by Professor Russell and the writer. Whereas the energy of molecular bombardments is characteristic of the temperature T, the spectral distribution of radiant energy is not, since it is present as an outward flux, from the hotter interior through the selectively absorbing photosphere. Various factors, such as abundance, atomic weight, and chemical affinity, may determine the extent to which any element in the chromosphere is shielded from radiation of its own resonance type by the "blanketing"

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[*] Phil. Mag. xl. pp. 472, 809 (1920).

[†] Astrophys. Jour., *in print*.

layers of this element in the photosphere. The Fraunhofer spectrum proves this "blanketing" effect. Sodium, in the chromosphere, is subject to radiation which is deficient in those particular wave-lengths which could put its atoms into an abnormal state, whereas the effective wave-lengths for barium are present. The effect of those types of radiation present in the Sun's chromosphere is equivalent, therefore, to a lower effective temperature or to a higher effective ionization potential for sodium than for barium.

Thus, Saha's treatment of the chromosphere as a black body is but an approximation to the actual conditions, and variations from the results of his treatment may be expected because of the deficiencies in particularly effective types of radiation as shown by the Fraunhofer spectrum.

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LXII. *On the Resistance of Electrolytes at High Frequencies.* *By* JOHN J. DOWLING, *M.A.*, *F.Inst.P.*, *and* KATHARINE M. PRESTON*.

§ 1. THE primary object of the experiments described in this paper was to ascertain whether the resistance of electrolytes is the same at high frequencies as for direct currents. The problem was attacked as far back as 1889 by Professor (now Sir) J. J. Thomson †. He used a Hertz oscillating circuit, and showed that at frequencies of the order of $10^8 \sim$ there was good reason to believe that the ohmic resistances of electrolytes were unchanged. As he pointed out, there is an element of difficulty in reconciling these facts with the ionic theory of electrolytic conduction. The problem, therefore, seemed worth further investigation, particularly in view of the fact that we had devised very accurate methods for measuring resistances at high frequencies.

§ 2. These methods are developments of principles made use of by the senior author in another connexion ‡.

The earlier experiments were carried out with a view to testing the possibilities of the methods contemplated, and it will, therefore, be convenient to describe the experiments

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* Communicated by Prof. J. Joly, F.R.S.

† Proc. Roy. Soc. vol. xlv., January 1889.

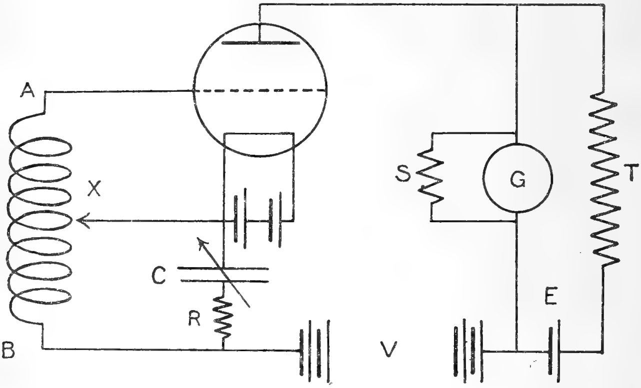
‡ "A direct-reading Ultramicrometer," Proc. Roy. Dublin Soc. xvi. p. 185, March 1921; also Brit. Assoc., Edinburgh Meeting, 1921.

more or less in the order they were made. The time at our disposal for the work did not, unfortunately, permit of the observations being pushed to the highest possible accuracy, but it will be evident that the new methods lend themselves to measurements of considerable precision.

§ 3. After several trials of various possible oscillation-circuits, and with different values of battery voltages, etc., the following was adopted as most likely to prove satisfactory for the present purpose. It was made up of existing apparatus, and could, no doubt, be much improved.

The coil AB (fig. 1) was of 170 turns bare (22) copper wire, wound on a 10 cm. square section frame 60 cms. long. C was a graduated sector condenser (100–1200 $\mu\mu$ farad), An Ediswan (ES$_4$) valve was employed with a ·6 ampere filament current. An anode battery of 20 volts was found suitable.

Fig. 1.



A potential balancing arrangement, inserted in the anode circuit, enables a sensitive galvanometer to be employed to detect small variations of the anode current.

The resistance to be measured is inserted in the oscillation-circuit at R, where it has no direct-current component passing through it.

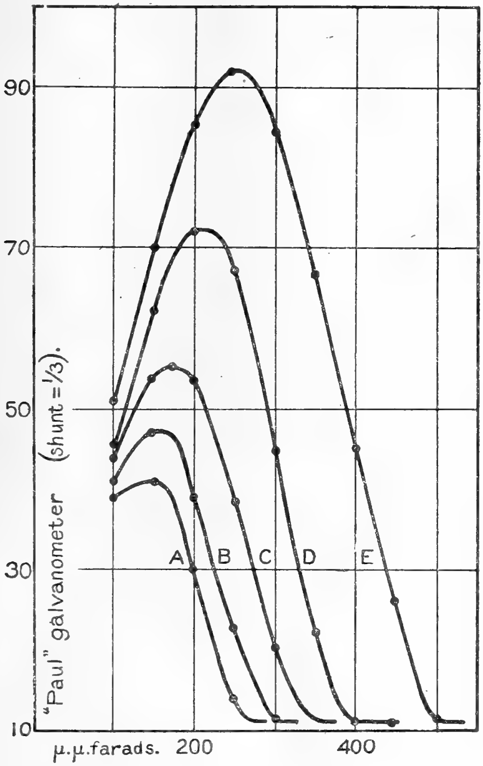
§ 4. The potential balancing device, just referred to, is represented by ET (fig. 1), and the theory of its action is important. It consists of a few cells (E), in series with a rather large resistance (T), the whole being in parallel with the galvanometer branch (GS). Let g be the resistance of the (shunted) galvanometer (GS).

If I is any value of the anode current, a current

$\frac{T}{T+g}.(I-I_0)$ passes through the galvanometer branch where $I_0=\frac{E}{T}$. Thus for values of I in the neighbourhood of I_0, a galvanometer of high sensitivity can be used to measure slight deviations of I from the "Standard value" I_0.

§ 5. The application of this apparatus to the measurement of resistance will be clear from a consideration of the following experiments. By a series of preliminary adjustments of the coils AB, the apparatus (fig. 1) was made to yield an "anode-current . . . capacity" curve of the form shown in fig. 2.

Fig. 2.



An electrolytic resistance * was then introduced at R and the observations made with the electrodes at various distances apart. An examination of the resulting family of curves (fig. 2; A, B, C, D, E corresponding to 5, 4, 3, 2, 1 cms. of

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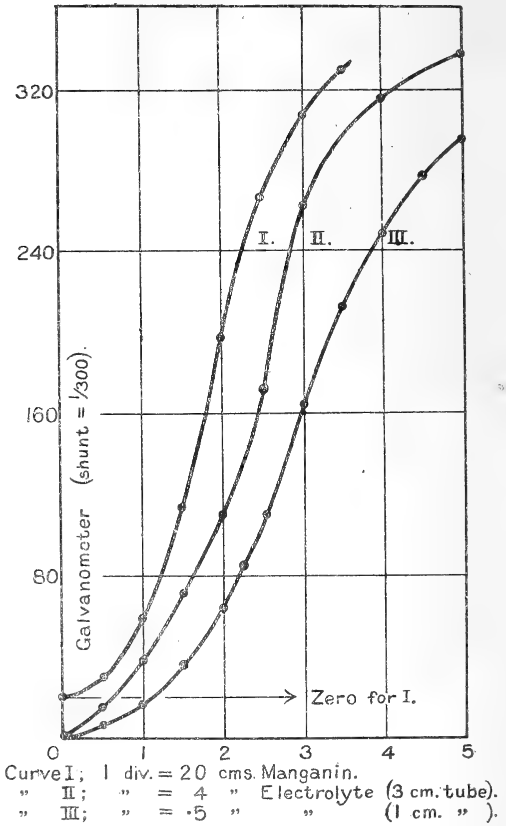
* A straight tube of $CuSO_4$ (Normal) with adjustable copper disk-electrodes.

electrolyte) shows that by confining our attention to a fixed value of the capacity (say, 150 $\mu\mu$ f.) the corresponding ordinates decrease by amounts nearly proportional to the increments of the resistance.

§ 6. Observations were now carried out on these lines, both with electrolytic resistances and with the practically non-inductive resistances afforded by lengths of No. 40 s.w.g. Manganin wire wound in small helices. The results of such observations are shown in fig. 3.

Fig. 3.



A comparison of the same resistances was then made by the Kohlrausch method, using a metre bridge. The following table shows the results.

Kohlrausch method :—

100 cms. wire has same resistance as 12·5 cms. of $CuSO_4$ sol. in 3 cm. tube.
,, .. ,, 1·0 ,, .. ,,

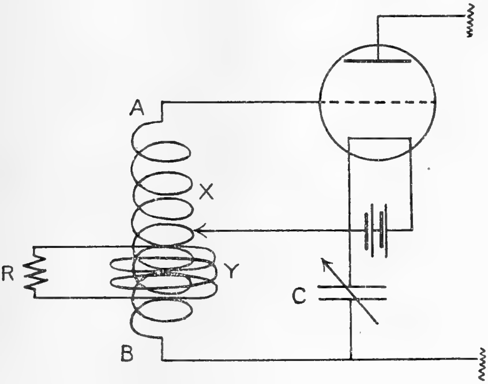
From fig. 3 :—

Galvanometer deflexion due to 100 cms. wire = 110 divisions.
" " " 12·5 " $CuSO_4$ in 3 cm. tube = 106 "
" " " 1·0 " " 1 " = 113 "

The discrepancy between the galvanometer readings is not as small as one would desire, but the Kohlrausch bridge arrangement available was rather unsatisfactory. Probably a considerable error is attributable to this.

§ 7. Since the curves in fig. 3 do not approximate, even along their middle parts, to straight lines, a trial of another circuit was made—namely, that shown in fig. 4. The resistance R to be measured is here introduced in series with a coil Y. This coil consisted of about 40 turns of No. 22 copper wound on a frame 25 cms. square. It was found best to place it coaxial with the coil AB and close to X. The oscillations of current in BCX then induce an oscillation in the circuit RY, and the amount of power contributed by the valve circuit for this purpose is a function of the resistance R. Figs. 5 and 6 show the variation of the anode current in the valve circuit as a function of R [*]. The curve (fig. 6) consists of two branches, that on the left (lower resistances) being almost perfectly straight for values of R up to about 400 ohms.

Fig. 4.



This circuit is suitable for the measurement of large as well as small resistances; but we shall confine ourselves to the latter at present.

§ 8. The *modus operandi* is as follows. Using suitable resistances of the fine Manganin wire, observations of the

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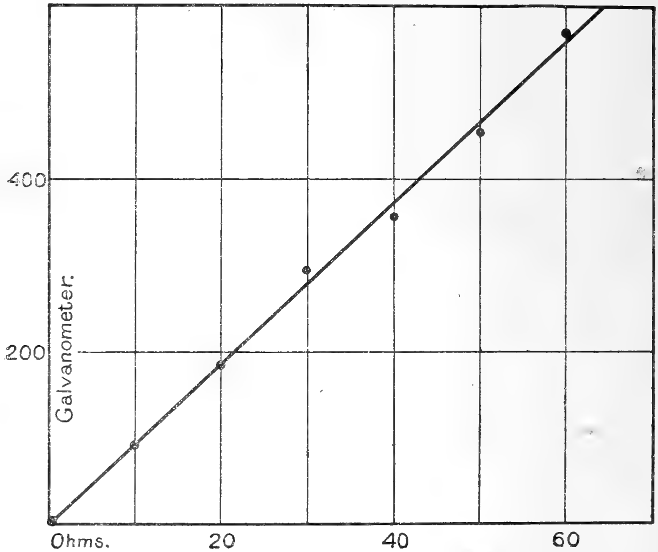
[*] The abscissæ in fig. 6 are lengths of a capillary tube of electrolyte: 1 cm. corresponds to 923 ohms.

galvanometer deflexion (shunted $\frac{1}{300}$) were made. A curve so obtained is shown in fig. 5 *. By a method of substitution the resistance of an electrolyte can be easily obtained ; but, to attain the highest accuracy, the following procedure is necessary.

§ 9. Having introduced the electrolytic resistance in the circuit RY, the resistance T is changed until the galvanometer is at zero. The galvanometer shunt S may then be reduced to unity and the galvanometer reading taken. Having restored the shunt S to a high value the electrolyte is removed, and, by means of a suitable set of non-inductive resistances, a resistance of nearly the same value is introduced at R in place of the electrolyte. On again reducing the galvanometer shunt a second reading is obtained. The difference between the two galvanometer readings is proportional to that between the electrolyte and the known resistance, in virtue of the linear relation shown in fig. 6. For calibration it is simply necessary to alter the known resistance by a small amount and to observe the effect on the galvanometer.

Fig. 5.



Great precision is obtainable in resistance determinations by this method. A consideration of fig. 5 shows this. The

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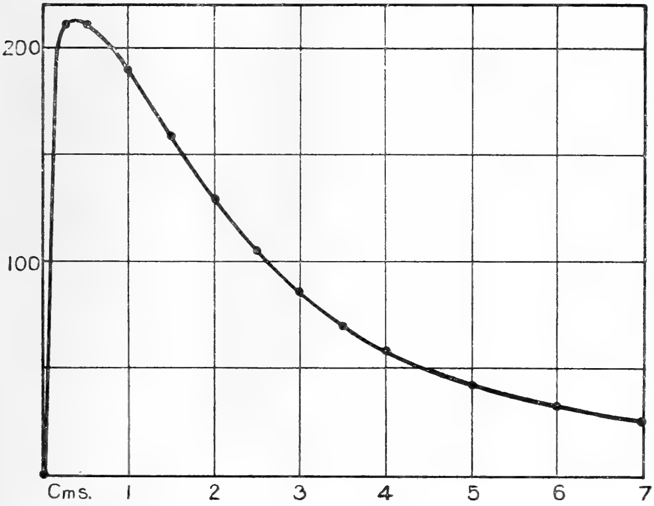
* The curve starts from zero because of the previous adjustment of the potential balancing device TE. Galvanometer sensitivity $=10^{-8}$ amp. per div.

observations were taken with the galvanometer shunted 300 times. The slope of the curve (left) is nearly 10 galvanometer divisions per ohm. In the balance method, the galvanometer being unshunted, one galvanometer division would clearly correspond to $\frac{1}{300}\times\frac{1}{10}$ or 3×10^{-4} ohm. In other words, in the measurement of a resistance of about 60 ohms an accuracy of 5 parts per million might be reached. For higher resistances the error would be less, but the method fails, of course, when the crest of the curve is reached.

§ 10. Fig. 6 indicates that, when the resistance R (fig. 4) is increased sufficiently, the anode current in the valve-circuit commences to decrease regularly. Although the relation between the anode current and R is not linear, it is, of course, clear that high resistances can be measured in much the same way as that described in § 9 for the smaller ones.

Fig. 6.



This method was therefore employed to investigate the high frequency resistances of glycerine solutions of copper sulphate. Gilmour *, who investigated these solutions, found that the specific resistance (for D.C.) varied irregularly with the concentration over a certain range ; Jones and others have described similar effects in other glycerine solutions. It is, of course, of some interest to determine whether these irregularities reproduce themselves at high frequencies.

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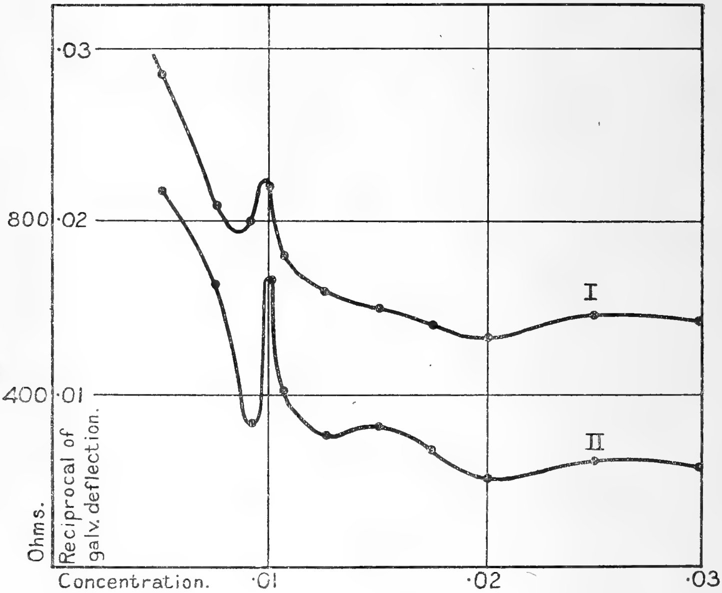
* Phil. Mag., March 1921.

§11. These solutions were of such high resistance that it was necessary to use a container of what would be rather an unsuitable design for high frequency work—particularly as the solutions were such poor conductors. The electrolyte was contained in a shallow copper vessel with a flat bottom (8 cms. diameter), which formed one electrode. The other electrode (copper disk 6 cms. diam.) was suitably supported from an accurately fitting wooden cover, so that it was $\frac{1}{2}$ cm. above the bottom electrode*. A galvanometer circuit, as described by Gilmour (*loc. cit.*) was used for the determination of the direct current resistance.

Fig. 7.



Having prepared a series of solutions covering the range of concentrations where anomalies occur, the container just described was filled in turn with each of them and observations taken, first with it inserted in the D.C. circuit and immediately afterwards in the H.F. circuit. Curves I. and II. (fig. 7) show the results so obtained. In Curve I., which refers to the D.C. experiment, the ordinates are proportional to the resistance *plus* a constant.

§ 12. The two curves closely resemble one another, but are

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* The vessel had appreciable capacity due to the size and proximity of the electrodes.

not quite identical, the H.F. Curve II. showing a much more pronounced "kink." It is unfortunate that the time at our disposal was insufficient to enable this problem to be subjected to a more careful examination. It is doubtful whether this discrepancy is due to an inherent defect in the methods of observation or whether there is actually here a difference between the H.F. and D.C. resistances. We hope to pursue the inquiry at another time.

Summary.

Methods of utilising H.F. oscillation valve-circuits for the the measurement of resistance have been devised, the principles involved being extensions of the senior author's "ultra-micrometer" circuits. These methods are capable of great precision and are suitable both for metallic and electrolytic resistances.

Preliminary tests indicate that ordinary electrolytes offer the same resistance to high * as well as to low frequency currents.

Observations on glycerine solutions, which show anomalous "resistance-concentration" variations for D.C., are somewhat inconclusive, but seem to show this to be more pronounced under H.F. conditions.

It is hoped to continue the work, especially at still higher frequencies and in connexion with the anomalous effects in glycerine solutions.

University College, Dublin.
Aug. 25, 1921.

LXIII. *A Graphical Synthesis of the Linear Vector Function.* *By* Prof. FREDERICK SLATE †.

PREVAILING use of the polygon-graph employs the same scale for the resultant, and throughout any group of its components. But the resultant can be expressed more comprehensively and still simply, when an individual scale-factor is allotted to each constituent vector. This idea is found to open an approach to linear vector

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* The frequency used was about three-quarters of a million. Even at this frequency the "skin effect" is negligible in such poor conductors.

† Communicated by the Author.

functions that is in some respects supplementary to the traditional methods and more direct *.

Let (O) be a base-point for three vectors ($\mathbf{V}_1$, $\mathbf{V}_2$, $\mathbf{V}_3$). Suppose them physically homogeneous (compoundable) and mutually perpendicular. Their union to a resultant ($\mathbf{V}$) drawn from (O) is shown fundamentally in terms of unit-vectors and their tensors by

$$\mathrm{V}\mathbf{v} \equiv \mathrm{V}_1\mathbf{v}_1 + \mathrm{V}_2\mathbf{v}_2 + \mathrm{V}_3\mathbf{v}_3. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The unit-vectors ($\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_3$) in this order of their indices may fit either cycle—right-handed or left-handed. Tensors cannot be negative under a primary ruling that every vector shall be rated positive in its own "forward" direction. This agrees, moreover, with algebraic usage regarding the radius vector of polar coordinates, and the perpendicular from the origin to any plane. Negative tensors are attendant later upon the algebra of assembling vector elements parallel to the same line, after giving them a unit-vector in common. The reversed (neutralizing) vector ($-\mathbf{V}$) can be described equally well both ways:

$$\left.\begin{aligned} (-\mathrm{V})\mathbf{v} &\equiv (-\mathrm{V}_1)\mathbf{v}_1 + (-\mathrm{V}_2)\mathbf{v}_2 + (-\mathrm{V}_3)\mathbf{v}_3\,; \\ \mathrm{V}\mathbf{v}' &\equiv \mathrm{V}_1\mathbf{v}_1' + \mathrm{V}_2\mathbf{v}_2' + \mathrm{V}_3\mathbf{v}_3'\,; \\ \mathbf{v}+\mathbf{v}' = \mathbf{v}_1+\mathbf{v}_1' &= \mathbf{v}_2+\mathbf{v}_2' = \mathbf{v}_3+\mathbf{v}_3' \equiv 0. \end{aligned}\right\} \quad . \quad . \quad (2)$$

Note that the cycle (circulation-rule for axial vectors), with the same index-order, must exchange between right-handed and left-handed at passage from ($\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_3$) to ($\mathbf{v}_1'$, $\mathbf{v}_2'$, $\mathbf{v}_3'$) or *vice versa*. Represent ($\mathbf{V}_1$, $\mathbf{V}_2$, $\mathbf{V}_3$) graphically by the arbitrary lengths ($\mathrm{OA} \equiv x_1\mathbf{v}_1$, $\mathrm{OB} \equiv y_1\mathbf{v}_2$, $\mathrm{OC} \equiv z_1\mathbf{v}_3$) associated with the scale-factors (a, b, c) such that

$$\left.\begin{aligned} \mathbf{V} &\equiv (ax_1)\mathbf{v}_1 + (by_1)\mathbf{v}_2 + (cz_1)\mathbf{v}_3\,; \\ \text{and consequently,}\quad -\mathbf{V} &\equiv (ax_1)\mathbf{v}_1' + (by_1)\mathbf{v}_2' + (cz_1)\mathbf{v}_3'. \end{aligned}\right\} \quad (3)$$

As a standard, all six factors of ($\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_3$) will be positive; but consistent algebra covers the usual variations. Let ($\mathbf{V}$) cut the plane of (ABC) at (R), the foot of the normal from

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* The generalized construction belongs to the older developments for centre of inertia. Its essential thought is carried back to Leibnitz by Minchin: 'Statics,' vol. i. p. 18 (1884). It is given bare recognition in recent books, but is scarcely made of any important service. See Greaves, 'Elementary Statics,' p. 19 (1886); Love, 'Theoretical Mechanics,' p. 15 (1897). Its control over scale-factors adapts it well to "contraction hypotheses," adding a resource there.

(O) to that plane be (N), and (S) the centre of figure of the triangle. With notation

$$\mathrm{OR}\equiv\mathbf{r},\quad \mathrm{ON}\equiv\mathbf{n},\quad \mathrm{NR}\equiv\mathbf{u},\quad \mathrm{OS}\equiv\mathbf{s},\quad \mathrm{SR}\equiv\mathbf{k},\quad . \quad (3\,a)$$

the quoted proposition leads to

$$\frac{\mathbf{V}}{a+b+c}=\mathbf{r}\equiv\mathbf{n}+\mathbf{u}\equiv\mathbf{s}+\mathbf{k}, \quad . \quad . \quad . \quad . \quad (4)$$

where on clearing of fractions the last members revert to using the composition with one scale-factor $(a+b+c)$; a vectorial addition is visualized without distortion in the graph. To locate the intersection (R), take (D) in (AB) satisfying $(\mathrm{AD}/\mathrm{DB}=b/a)$; the line (CD) contains (R), the ratio of segments being $(\mathrm{DR}/\mathrm{RC}=c/(a+b)$. Hence with given intercepts (x_1, y_1, z_1) the direction of $(\mathbf{V})$ is fixed by two ratios ; the magnitudes of their terms do not enter. Planes parallel to (ABC) preserve these ratios, and only magnify its graph by changing the sum $(a+b+c)$. This segregation is a working convenience.

Next particularize on making (OA, OB, OC) the unit-vectors themselves. Since here $(x_1=y_1=z_1=1)$, the scale-factors (a, b, c) become numerically the tensors $(\mathrm{V}_1, \mathrm{V}_2, \mathrm{V}_3)$. It is common practice that the latter shall include every dimensional adjustment. Distinguish the special values of $(3\,a)$ as $(\mathbf{r}', \mathbf{n}', \mathbf{u}', \mathbf{s}', \mathbf{k}')$, and remark that $(\mathbf{n}'\equiv\mathbf{s}', \mathbf{u}'\equiv\mathbf{k}')$ because (N, S) now coincide. Choose $(\mathbf{w}'\equiv w'\mathbf{w}_1')$ at right-angles with $(\mathbf{u}')$ in the present plane (ABC) ; $(\mathbf{n}', \mathbf{u}')$ are perpendicular, and another correct general form for $(\mathbf{V})$ follows, provided that the tensor (w') is given proper magnitude and dimensions :

$$\mathbf{V}=(\mathrm{V}_1+\mathrm{V}_2+\mathrm{V}_3)(\mathbf{n}'+\mathbf{u}')=(\mathrm{V}_1+\mathrm{V}_2+\mathrm{V}_3)\left[\mathbf{n}'+(\mathbf{n}'\times\mathbf{w}')\right]. \quad . \quad . \quad . \quad (5)$$

With the indicated order of factors $(\mathbf{n}', \mathbf{w}')$, accept the separation in the second member as conforming more closely to physical data. Then $(\mathbf{w}')$ is a merely mathematical auxiliary, whose sense in its line must be governed by either one convention or the other concerning circulation ; $(\mathbf{w}')$ must be reversed at transition between right-handed cycle and left-handed. But should the third member register the primary record of physics through its variables and its form, the alternatives regarding assumed circulation clearly reverse $(\mathbf{u}')$. As though, *without changing the circulation-rule*, we came to deal with a new vector by applying the same scale-factor to $(\pm\mathbf{u}')$,

$$\mathbf{V}''\equiv(V_1+V_2+V_3)\,[\mathbf{n}'-(\mathbf{n}'\times\mathbf{w}')]=(V_1+V_2+V_3)(\mathbf{n}'-\mathbf{u}'), \quad . \; . \; . \quad (6)$$

convertible into $(\mathbf{V})$ by imposing the new convention. The last member involves a different intersection with the same (ABC), marked by

$$\mathbf{r}''\equiv\mathbf{n}'+\mathbf{u}''=\frac{\mathbf{V}''}{V_1+V_2+V_3} \quad [\mathbf{u}'+\mathbf{u}''\equiv 0]. \quad . \quad (7)$$

This conical symmetry of $(\mathbf{r}, \mathbf{r}'')$ relative to an axis $(\mathbf{n}')$ secures equal tensors (V, V''). Such opposed behaviour of linear and axial vectors towards change of cycle is inherent in separable assignments of axes and of their cycle-order.

To illustrate how the above discrimination affects mixed conditions, subdivide $(\mathbf{w}')$ into a mathematical auxiliary $(\mathbf{w}'')$ and a physical vector $(\mathbf{w})$. Let $(\mathbf{L}', \mathbf{A}')$ express the physical facts about linear and axial contributions to $(\mathbf{V})$, additive under its rule ; so that

$$\mathbf{V}\equiv\mathbf{L}'+\mathbf{A}'\equiv(V_1+V_2+V_3)[\mathbf{n}'+(\mathbf{n}'\times\mathbf{w}'')] + [(V_1+V_2+V_3)(\mathbf{n}'\times\mathbf{w})]. \quad . \quad (8)$$

A change to the other rule, on whatever grounds executed, is to be offset in $(\mathbf{L}')$ through reversal of $(\mathbf{w}'')$ as a detail of mathematical routine ; the determinate physical element $(\mathbf{w})$ can only persist in direction, making thus the last term negative. Then having

$$\mathbf{V}'\equiv\mathbf{L}'-\mathbf{A}' \;;\quad \mathbf{V}-2\mathbf{A}'=\mathbf{V}' \;;\quad \tfrac{1}{2}(\mathbf{V}+\mathbf{V}')=\mathbf{L}' \;;\quad \tfrac{1}{2}(\mathbf{V}-\mathbf{V}')=\mathbf{A}' ; \quad . \; . \; . \quad (9)$$

$(\mathbf{V}, \mathbf{V}')$ are mutually convertible on the basis explained for $(\mathbf{V}, \mathbf{V}'')$. Their sum is purely linear, and their difference purely axial. Whatever is superficially ambiguous in really occurring cases must be removed by exploration of phenomena, in order to disentangle $(\mathbf{w}'', \mathbf{w})$.

Adopt $(\mathbf{v}_1/3, \mathbf{v}_2/3, \mathbf{v}_3/3)$ for coordinates of (N), and resolve $(\mathbf{w}')$ of equation (5) as shown by

$$\mathbf{w}'\equiv w_1\mathbf{v}_1+w_2\mathbf{v}_2+w_2\mathbf{v}_3. \quad . \; . \; . \; . \; . \quad (10)$$

The suppositions include perpendicularity of $(\mathbf{n}', \mathbf{w}')$, which implies one negative tensor or more in the last equation. The group $(\mathbf{V}_1, \mathbf{V}_2, V_3)$ and corresponding components of $(\mathbf{V}'')$, written in parallel expansion on either background outlined under equations (5, 6, 8), appear as

$$\left.\begin{aligned} \mathbf{V}_1 &= \tfrac{1}{3}(\mathrm{V}_1+\mathrm{V}_2+\mathrm{V}_3)\left[\mathbf{v}_1+(v_2w_3-v_3w_2)\mathbf{v}_1\right]; \\ \mathbf{V}_1'' &= \tfrac{1}{3}(\mathrm{V}_1+\mathrm{V}_2+\mathrm{V}_3)\left[\mathbf{v}_1-(v_2w_3-v_3w_2)\mathbf{v}_1\right]; \\ &\text{etc., etc.} \end{aligned}\right\} \quad (11)$$

The insertion of the unit-tensors (v_1, v_2, v_3) preserves the formal type ready for algebraic evaluation. These preliminaries have broadly suggestive aspects: the conversions of $(\mathbf{n}')$ into $(\mathbf{V}, \mathbf{V}', \mathbf{V}'')$ are after the pattern of stretch-operators and quaternions, for instance. But equations (5) to (9) also place a patent emphasis upon taking due account of axial combinations with the operand-vector, if $(\mathbf{V}, \mathbf{V}', \mathbf{V}'')$ become generally representative of linear vector functions and of relations among them. This is for the present our chief concern.

Return accordingly to equation (4) and repeat the above sequence, modified only as that more general form demands. Begin with the arbitrary partitions, which may finally be algebraic sums,

$$a \equiv a_1 + a_2; \quad b \equiv b_1 + b_2; \quad c \equiv c_1 + c_2; \; . \; . \quad (12)$$

and express $(\mathbf{V})$ to match their terms:

$$\begin{aligned} \mathbf{V} \equiv &\left[(a_1x_1)\mathbf{v}_1 + (b_1y_1)\mathbf{v}_2 + (c_1z_1)\mathbf{v}_3\right] \\ &+ \left[(a_2x_1)\mathbf{v}_1 + (b_2y_1)\mathbf{v}_2 + (c_2y_1)\mathbf{v}_3\right] \equiv \mathbf{Q}_1 + \mathbf{Q}_2. \end{aligned} \quad (13)$$

The components $(\mathbf{Q}_1, \mathbf{Q}_2)$ are given by means of the same intercepts; their graphs utilize the same plane (ABC), though scale-factors are varied. Make equation (4) model and put

$$\left.\begin{aligned} \mathbf{Q}_1 &= (a_1+b_1+c_1)\mathbf{r}_1 \equiv (a_1+b_1+c_1)(\mathbf{n}+\mathbf{u}_1) \equiv (a_1+b_1+c_1)(\mathbf{s}+\mathbf{k}_1); \\ \mathbf{Q}_2 &= (a_2+b_2+c_2)\mathbf{r}_2 \equiv (a_2+b_2+c_2)(\mathbf{n}+\mathbf{u}_2) \equiv (a_2+b_2+c_2)(\mathbf{s}+\mathbf{k}_2). \end{aligned}\right\} \quad (14)$$

The arbitrary character of $(\mathbf{Q}_1, \mathbf{Q}_2)$ enters their geometry through the elements $(\mathbf{u}_1, \mathbf{u}_2, \mathbf{k}_1, \mathbf{k}_2)$, since $(\mathbf{n}, \mathbf{s})$ belong to both. We can treat $(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2)$ as making real intersections with the plane (ABC), whose equation their extremities satisfy, which yields useful corollaries. The recomposition of $(\mathbf{Q}_1, \mathbf{Q}_2)$, by applying to the second members the general construction detailed specially for equations (3, 4), is simple to verify. The third members reproduce the scheme of equation (5), and justify as general expressions

$$\left.\begin{aligned}\mathbf{Q}_1&=(a_1+b_1+c_1)\left[\mathbf{n}+(\mathbf{n}\times\mathbf{w}_1)\right];\\ \mathbf{Q}_2&=(a_2+b_2+c_2)\left[\mathbf{n}+(\mathbf{n}\times\mathbf{w}_2)\right];\end{aligned}\right\}\quad .\ .\ .\ (15)$$

where $(\mathbf{w}_1, \mathbf{w}_2)$ successively replace $(\mathbf{w}')$. Obviously, the ideas underlying equations (8, 9) continue into this phase, which enables us to indicate compactly a conversion of $(\mathbf{n})$ into any complementary constituents of $(\mathbf{V})$. And when a mean vector $(\overline{\mathbf{w}})$ has been determined from

$$(a+b+c)\overline{\mathbf{w}}\equiv(a_1+b_1+c_1)\mathbf{w}_1+(a_2+b_2+c_2)\mathbf{w}_2\ ;\quad \mathbf{u}\equiv\mathbf{n}\times\overline{\mathbf{w}}\ ;\quad .\ .\ .\ (16)$$

$(\mathbf{Q}_1, \mathbf{Q}_2)$ can be summed into

$$\mathbf{V}=(a+b+c)\left[\mathbf{n}+(\mathbf{n}\times\overline{\mathbf{w}})\right].\quad .\ .\ .\ (17)$$

But an attempt at similar general conversion of $(\mathbf{s})$ into $(\mathbf{Q}_1, \mathbf{Q}_2, \mathbf{V})$ halts at the possible obliquity to $(\mathbf{s})$ of $(\mathbf{k}_1, \mathbf{k}_2, (\mathbf{k}))$. The situation that involves mean vectors $(\mathbf{s}, \overline{\mathbf{w}})$ to this extent dislocated, remains for analysis after taking out three particular cases. First, the mean vector $(\overline{\mathbf{w}})$ may prove to vanish; $(\mathbf{V}, \mathbf{n})$ become colinear. Or $(\mathbf{s})$ can be perpendicular to $(\mathbf{k})$, though oblique to each separate part. Or again, $(\mathbf{s})$ can be perpendicular to both $(\mathbf{k}_1, \mathbf{k}_2)$, yet not coincident with $(\mathbf{n})$. If for the then colinear sum the relation among tensors be added:

$$k_1(a_1+b_1+c_1)+k_2(a_2+b_2+c_2)\equiv k(a+b+c)\ ;\quad\text{and}\quad \mathbf{k}\equiv\mathbf{s}\times\mathbf{q},\quad .\ .\ .\ (18)$$

with permissibly oblique factors, the type of equation (17) is retained by

$$\mathbf{V}\equiv\mathbf{Q}_1+\mathbf{Q}_2=(a+b+c)\left[\mathbf{s}+(\mathbf{s}\times\mathbf{q})\right],\quad .\ .\ (19)$$

whose peculiar lesson is more fully read later.

Under natural guidance of several aspects in the foregoing results, reserve one component (say $(\mathbf{Q}_1)$) as stated for equation (13), and transform $(\mathbf{Q}_2)$ for general discussion through the equivalents

$$\left.\begin{aligned}(a_2x_1)\mathbf{v}_1&\equiv(y_1\mathbf{v}_2+z_1\mathbf{v}_3)\times(\mathrm{Y}_1\mathbf{v}_2+\mathrm{Z}_1\mathbf{v}_3)=(y_1\mathrm{Z}_1-z_1\mathrm{Y}_1)\mathbf{v}_1\ ;\\ (b_2y_1)\mathbf{v}_2&\equiv(z_1\mathbf{v}_3+x_1\mathbf{v}_1)\times(\mathrm{Z}_2\mathbf{v}_3+\mathrm{X}_2\mathbf{v}_1)=(z_1\mathrm{X}_2-x_1\mathrm{Z}_2)\mathbf{v}_2\ ;\\ (c_2z_1)\mathbf{v}_3&\equiv(x_1\mathbf{v}_1+y_1\mathbf{v}_2)\times(\mathrm{X}_3\mathbf{v}_1+\mathrm{Y}_3\mathbf{v}_2)=(x_1\mathrm{Y}_3-y_1\mathrm{X}_3)\mathbf{v}_3.\end{aligned}\right\}\ (20)$$

The vector products employ first factors that are distances from the lines of $(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3)$, and that combine significantly as projections into the radius vector linking with equation (4),

$$x_1\mathbf{v}_1+y_1\mathbf{v}_2+z_1\mathbf{v}_3=3\mathbf{s}. \quad . \quad . \quad . \quad . \quad (21)$$

This diagonal from (O) of the parallelopiped $(x_1y_1z_1)$, determined by given axis-intercepts, takes prominent place among the data. The second factor in each vector product is seen to specify legitimately a vector parallel to a coordinate *plane*, $(Y_1, Z_1, Z_2, X_2, X_3, Y_3)$ being adjusted positive magnitudes. Because $(\mathbf{Q}_2)$ is arbitrary, the third members must be independent; which bars their general union into one vector product of which $(3\mathbf{s})$ is a factor. Observe that the specifications parallel to the coordinate *axes* in this group amount in the aggregate to

$$(X_2+X_3)\mathbf{v}_1+(Y_1+Y_3)\mathbf{v}_2+(Z_1+Z_2)\mathbf{v}_3\equiv\mathbf{A}. \quad . \quad (22)$$

Further, since every such summation by planes effectively takes each component by axes twice, the last requirement can be met as a total with

$$\tfrac{1}{2}\mathbf{A}=\frac{X_2+X_3}{2}\mathbf{v}_1+\frac{Y_1+Y_3}{2}\mathbf{v}_2+\frac{Z_1+Z_2}{2}\mathbf{v}_3, \quad . \quad (23)$$

assigning components to axes. On the face of it, this substitutes an average, and effaces some particulars of equation (20). The latter can be summed into these terms:

$$\mathbf{Q}_2=[3\mathbf{s}\times\mathbf{A}]-[(y_1Z_2-z_1Y_3)\mathbf{v}_1 \\ +(z_1X_3-x_1Z_1)\mathbf{v}_2+(x_1Y_1-y_1X_2)\mathbf{v}_3]\,; \quad . \quad (24)$$

an important result that we put into the condensed notation,

$$\mathbf{Q}_2=\mathbf{M}\mp\mathbf{Q}_2'\,; \quad \mathbf{Q}_2+\mathbf{Q}_2'=\mathbf{M}\,; \quad \mathbf{Q}_2=\mathbf{M}+\mathbf{Q}_2''\,; \quad \mathbf{Q}_2'+\mathbf{Q}_2''\equiv 0\,; \\ . \quad . \quad . \quad (25)$$

where the double sign has been made to allow $(\mathbf{M}, \mathbf{Q}_2)$ as alternates for the resultant diagonal. Evidently $(\mathbf{Q}_2')$ admits a new sum of vector products:

$$\mathbf{Q}_2'=[(y_1\mathbf{v}_2+z_1\mathbf{v}_3)\times(Y_3\mathbf{v}_2+Z_2\mathbf{v}_3)] \\ +[(z_1\mathbf{v}_3+x_1\mathbf{v}_1)\times(Z_1\mathbf{v}_3+X_3\mathbf{v}_1)] \\ +[(x_1\mathbf{v}_1+y_1\mathbf{v}_2)\times(X_2\mathbf{v}_1+Y_1\mathbf{v}_2)]. \quad . \quad . \quad (26)$$

The first factors throughout $(\mathbf{Q}_2, \mathbf{Q}_2')$ are identical, and the average fixed by equation (23) reappears; though in general the distributions differ, since the second factors of $(\mathbf{Q}_2, \mathbf{Q}_2')$ contain pairs that are complementary within $(\mathbf{A})$. Continuing to coordinate the graphs through the plane (ABC), other scale-factors applied to the same (x_1, y_1, z_1) give

$$\left.\begin{aligned} \mathbf{Q}_2'' &\equiv (a_2'x_1)\mathbf{v}_1 + (b_2'y_1)\mathbf{v}_2 + (c_2'z_1)\mathbf{v}_3 \equiv (a_2' + b_2' + c_2')\mathbf{r}_2''; \\ \mathbf{M} \equiv \mathbf{Q}_2 - \mathbf{Q}_2'' &= (a_2 - a_2')x_1\mathbf{v}_1 + (b_2 - b_2')y_1\mathbf{v}_2 + (c_2 - c_2')z_1\mathbf{v}_3. \end{aligned}\right\} \quad (27)$$

Thus the vanishing of $(\mathbf{M})$ depends upon the equality in pairs of tensors for the components of $(\mathbf{Q}_2, \mathbf{Q}_2'')$. Also $(\mathbf{M})$ serves as a measured consequence of unequal scale-factors there, on reduction to the same (ABC), through whatever circumstances such differences come into question.

The indications of reversal by equations (2) have *prima facie* validity. Yet on proceeding to the algebraic equivalents for $(-\mathbf{V})$ in equations (3), an issue of fact will nevertheless be raised: Whether phenomena harmonize with making freely exchangeable, as related to the first forms, the specific factorings in

$$\left.\begin{aligned} -\mathbf{V} &= a(-x_1\mathbf{v}_1) + b(-y_1\mathbf{v}_2) + c(-z_1\mathbf{v}_3), \\ -\mathbf{V} &= (-a)(x_1\mathbf{v}_1) + (-b)(y_1\mathbf{v}_2) + (-c)(z_1\mathbf{v}_3). \end{aligned}\right\} \quad (28)$$

Where physical properties sanction the first equation, they legitimize at once unaltered scale-factors, to be partners of what the reversed vector $(-3\mathbf{s})$ stands for more widely. This holds for coefficients that belong to a line, and not to one direction in it; moment of inertia and light-speed in crystals are instances. The other equation refers more at first-hand to opposed states like stretch and squeeze. The proved precision of either equality leads to decisive inferences in other directions. The consideration of such matters, for which equations (13, 14, 25) may offer a starting-point, bears upon classifying linear vector functions, especially as regards conjugate pairs. The operand of the function that here builds up $(\mathbf{V})$ was indeed defined particularly by equation (21). However, with (x_1, y_1, z_1) of equations (3) selected at will, and adopting the superpositions proved for principal axes, the procedure enlarges itself at this stage into treating functions of any vector, whose components $(x_1\mathbf{v}_1, y_1\mathbf{v}_2, z_1\mathbf{v}_3)$ will then be chosen to represent. Primarily by using *for the operand* some one scale-factor (planes parallel to (ABC)), though the algebra may be shaped to break down that restriction. The developments are adaptable to whichever $(3\mathbf{s})$ the working basis best yields, bearing in mind about two differing scales, that either may be norm for the other's distortion. It is true that equations (14) are perhaps simpler for $(\mathbf{n})$, another standard parameter of a plane. Still the initiative at $(\mathbf{s})$ or $(\mathbf{n})$ will always be weighted in favour of expressing physics; a mathematical gain is less fruitful. A thought that governs, too, the parallel sequences within ellipsoidal geometry that have the same graphical origin, and that have long been exploited.

The derivation of ($\mathbf{M}$) has led to an invariant form, that makes ($\mathbf{Q}_2 - \mathbf{Q}_2''$) necessarily perpendicular to the mean vector ($\mathbf{s}$), the second factor in the vector product being their common value of ($\mathbf{A}$). Otherwise the invariance is to be delimited in the light of equations (14, 27). Therefore every combination whose net sum is expressible by ($\mathbf{M}$) must at least be self-cancelling in the line of ($\mathbf{s}$); the factor ($\mathbf{A}$) preserves for ($\mathbf{M}$) a margin of flexibility proper to all vector products. Observe how well all these features align with the specialized equation (19). This mode of statement adapts ($\mathbf{M}$) to embody the dominant difference between a pair of "conjugate vectors," according to standard usage of that term. For if we define a companion to ($\mathbf{V}$) by

$$\mathbf{V}' \equiv \mathbf{V} - \mathbf{M} = \mathbf{Q}_1 + \mathbf{Q}_2'', \quad . \quad . \quad . \quad . \quad (29)$$

($\mathbf{Q}_2$) has been replaced with ($\mathbf{Q}_2''$). Then bring out further the mutually supplementary relation of ($\mathbf{V}'$, $\mathbf{V}$) to ($\mathbf{M}$) in the symmetry of

$$\mathbf{V} - \tfrac{1}{2}\mathbf{M} = \mathbf{Q}_1 + (\mathbf{Q}_2'' + \tfrac{1}{2}\mathbf{M}) \; ; \quad \mathbf{V}' + \tfrac{1}{2}\mathbf{M} = \mathbf{Q}_1 + (\mathbf{Q}_2 - \tfrac{1}{2}\mathbf{M}) \; ; \quad (30)$$

and compare with the usual established forms. By reference to equations (13, 20, 24), the nine coefficients in each set of the rectangular components for ($\mathbf{V}'$, $\mathbf{V}$) can be picked out, and their interchanges recognized at sight, which render this pair conjugate, ($\mathbf{Q}_1$) being common to both. Proceed to note that

$$\tfrac{1}{2}(\mathbf{V} + \mathbf{V}') = \mathbf{Q}_1 + \tfrac{1}{2}(\mathbf{Q}_2 + \mathbf{Q}_2'') \; ; \quad \tfrac{1}{2}(\mathbf{V} - \mathbf{V}') = \tfrac{1}{2}\mathbf{M} \; ; \quad (31)$$

showing complete formal resemblance to equations (9) through the obvious identifications with ($\mathbf{L}'$, $\mathbf{A}'$) in the latter. The application is quite direct, if inquiry has isolated an intrinsic axial constituent, as in electromagnetism; this treatment then acquires clear physical status immediately. But though equations (20) are less vital, if they merely prepare for deviations from equations (28) which simulate that experimental trend towards composite vectors, the artifice does not lose its value. It creates a widely comprehensive scheme[*]. What correlates

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[*] The range of the plan can be broadened usefully to cover a "complex" of non-homogeneous vectors, like forces and couples in a forcive impressed upon any system as related to the centre of inertia. Fusion into some analogue of screw-motion would follow easily. The track pursued has several contacts with Poinsot's force-transfer, which likewise turns upon shift of vectors to secure lever-arm. Our moment-vectors ($\mathbf{Q}_2$, $\mathbf{Q}_2''$, $\mathbf{M}$) drawn at (O) presuppose ($\mathbf{A}$) "off centre." The conditions underlying equations (34) below are not altogether remote from those of a couple.

both typical situations rather naturally under one point of view is the essential nexus made explicit for equations (2): Reversal of axes with retention of their identity (so to speak), makes abandonment of the original cycle inevitable. It is plain from what precedes how that mode of reversal would be carried through to any valid equivalent of

$$-(+\mathbf{V})=[(a_1x_1)\mathbf{v}_1'+(b_1y_1)\mathbf{v}_2'+(c_1z_1)\mathbf{v}_3'] \\ +[(a_2x_1)\mathbf{v}_1'+(b_2y_1)\mathbf{v}_2'+(c_2z_1)\mathbf{v}_3'], \quad . \quad (32)$$

intentionally emphatic of original direction as given by equation (1). Similarly, lay down $(\mathbf{v}_1', \mathbf{v}_2', \mathbf{v}_3')$ as *original unit-vectors* for $(+\mathbf{V}')$, and throw all necessary changes of scale-factor into the second term by compensations in the other term. Reversal now substitutes $(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3)$ and gives

$$-(+\mathbf{V}')=[(a_1x_1)\mathbf{v}_1+(b_1y_1)\mathbf{v}_2+(c_1z_1)\mathbf{v}_3] \\ +[(a_2'x_1)\mathbf{v}_1+(b_2'y_1)\mathbf{v}_2+(c_2'z_1)\mathbf{v}_3]. \quad . \quad (33)$$

Reference to equations (27) makes it plain that addition of equations (32, 33) has for result the negative of (**M**). The terms of the comparison inverted lead to (**M**) itself; the thought is the same and the end reached. Finally, it is important for the context to remark how (**M**) can change sign, the order of its factors being untouched. First by reversal of either factor separately; or secondly, by reversal of both factors, and transition to the other circulation-rule as well; or thirdly, by change of rule alone. Other bearings of the last possibility, on reversal of $(\mathbf{Q}_2, \mathbf{Q}_2'')$, are evident.

The device in equations (20) is prompted by the announced purpose that prefaces equations (12). But at this point its consequences are available to round out the method and also add some particulars about (**M**). Whenever $(\mathbf{Q}_2)$ is parallel to (ABC) by choice or necessity, $(\mathbf{r}_2)$ loses definiteness as first defined; every such case, however, is still tractable by means of a difference of two vectors drawn from (O). Let these be $(\mathbf{S}_1, \mathbf{S}_2)$, on which (ABC) makes intercepts $(\mathbf{s}_1, \mathbf{s}_2)$; the sum-diagonal $(\mathbf{S}_1+\mathbf{S}_2)$ cuts that plane at $(\boldsymbol{\rho}_1)$, while the difference-diagonal taken in the sense that gives its parallel at (O) a real intercept $(\boldsymbol{\rho}_2)$ is $(\mathbf{S}_1-\mathbf{S}_2)$. Consistently, within the generalized construction,

$$\mathbf{S}_1\equiv n_1\mathbf{s}_1\,;\quad \mathbf{S}_2\equiv n_2\mathbf{s}_2\,;\quad \mathbf{S}_1+\mathbf{S}_2=(n_1+n_2)\boldsymbol{\rho}_1\,;\quad \mathbf{S}_1-\mathbf{S}_2=(n_1-n_2)\boldsymbol{\rho}_2. \quad . \; . \; . \; . \quad (34)$$

So long as complete coincidence of $(\mathbf{S}_1, \mathbf{S}_2)$ is excluded, the last expression cannot vanish. It is indeterminately satisfied for $(n_1 = n_2 ;\ \rho_2 = \infty)$, which at once justifies the proposition and adds its necessary condition. It is to inspection true that a plane parallel to any difference-diagonal cuts off equally proportional segments of both components, and of their half-sum. In illustration, interpret what comes of combining equations (14, 25) and dividing by $(a_2 + b_2 + c_2)$:

$$\frac{\mathbf{M}}{a_2+b_2+c_2} = \frac{\mathbf{Q}_2}{a_2+b_2+c_2} - \frac{\mathbf{Q}_2''}{a_2+b_2+c_2} = \mathbf{p} = (\mathbf{s}+\mathbf{k}_2) - (\mathbf{s}+\mathbf{u}_2''). \quad . \quad . \quad . \quad (35)$$

The vector $(\mathbf{p})$ will be both perpendicular to $(\mathbf{s})$ and parallel to (ABC); $(\mathbf{Q}_2, \mathbf{Q}_2'')$ neutralize each other's components in $(\mathbf{s})$. If $(\mathbf{u}_2'')$ completes a rectangular decomposition of $(\mathbf{k}_2)$ in (ABC), it will lie in (SN) of $(3\,a)$; but $(\mathbf{p}, \mathbf{u}_2'')$ may be oblique. Of course the second member is valid throughout two groups of vectors, subject to a proviso of common difference between pairs. And again there is brought forward a reminder of equation (18).

Return to equations (27, 29, 30), whose parts $(\mathbf{Q}_2, \mathbf{Q}_2'')$ are less special than those supposed in equation (35). When $(a_2 + b_2 + c_2)$, $(a_2' + b_2' + c_2')$ are unequal, a common divisor does not "reduce $(\mathbf{Q}_2, \mathbf{Q}_2'')$ to the plane (ABC)"; some analysis of the latter relations is needed. Let the projections of $(\mathbf{r}_2, \mathbf{r}_2'')$ have tensors (x_2, y_2, z_2), (x_2'', y_2'', z_2''). Equating equivalents for each of $(\mathbf{Q}_2, \mathbf{Q}_2'')$, record the consequences

$$\left.\begin{aligned}
&(a_2+b_2+c_2)x_2 = a_2 x_1 ;\ (a_2'+b_2'+c_2')x_2'' = a_2' x_1, \text{ etc.};\\
&\frac{m_2}{m_2''} \equiv \frac{a_2+b_2+c_2}{a_2'+b_2'+c_2'} = \frac{a_2x_2''}{a_2'x_2} = \frac{b_2y_2''}{b_2'y_2} = \frac{c_2z_2''}{c_2'z_2}\\
&\qquad\qquad = \frac{a_2x_2''+b_2y_2''+c_2z_2''}{a_2'x_2+b_2'y_2+c_2'z_2};
\end{aligned}\right\} . \quad (36)$$

whose second and last members connect interchange of scale-factors with the ratio (m_2/m_2''). Because change of cycle cannot neglect it, that crossed pairing of intercepts $(\mathbf{r}_2, \mathbf{r}_2'')$ and scale-factors (m_2, m_2'') should be examined in some detail, and its bearing upon conjugate relation extracted. To this end, begin with two general vectors $(\mathbf{S}_1, \mathbf{S}_2)$ drawn from (O), and let $(\mathbf{R}_1, \mathbf{R}_2)$ be given by their inversion; so that in notation like equation (34),

$$\left.\begin{array}{c}\mathbf{R}_1 \equiv n_2\mathbf{s}_1\,; \quad \mathbf{R}_2 \equiv n_1\mathbf{s}_2\,; \quad \tfrac{1}{2}(\mathbf{R}_1+\mathbf{R}_2) \equiv n\boldsymbol{\rho}_1'\,; \\ \tfrac{1}{2}(\mathbf{R}_1-\mathbf{R}_2) \equiv (n_2-n_1)\boldsymbol{\rho}_2'.\end{array}\right\} \quad . \; . \quad (37)$$

The mean scale-factor (n) is common to $(\mathbf{S}_1+\mathbf{S}_2)$, $(\mathbf{R}_1+\mathbf{R}_2)$; but $(\boldsymbol{\rho}_1, \boldsymbol{\rho}_1')$ differ in general. Omitting steps of plain reduction, the working out shows

$$\left.\begin{array}{l}\tfrac{1}{2}(\mathbf{S}_1+\mathbf{S}_2)+\tfrac{1}{2}(\mathbf{R}_1+\mathbf{R}_2)=\tfrac{1}{2}(\mathbf{S}_1+\mathbf{R}_1)+\tfrac{1}{2}(\mathbf{S}_2+\mathbf{R}_2)=n(\mathbf{s}_1+\mathbf{s}_2)\,; \\ \tfrac{1}{2}(\mathbf{S}_1-\mathbf{S}_2)+\tfrac{1}{2}(\mathbf{R}_1-\mathbf{R}_2)=\tfrac{1}{2}(\mathbf{S}_1+\mathbf{R}_1)-\tfrac{1}{2}(\mathbf{S}_2+\mathbf{R}_2)=n(\mathbf{s}_1-\mathbf{s}_2)\,; \\ \tfrac{1}{2}(\mathbf{S}_1+\mathbf{S}_2)-\tfrac{1}{2}(\mathbf{R}_1+\mathbf{R}_2)=\tfrac{1}{2}(\mathbf{S}_1-\mathbf{R}_1)+\tfrac{1}{2}(\mathbf{S}_2-\mathbf{R}_2) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad =\dfrac{n_1-n_2}{2}(\mathbf{s}_1-\mathbf{s}_2)\,; \\ \tfrac{1}{2}(\mathbf{S}_1-\mathbf{S}_2)-\tfrac{1}{2}(\mathbf{R}_1-\mathbf{R}_2)=\tfrac{1}{2}(\mathbf{S}_1-\mathbf{R}_1)-\tfrac{1}{2}(\mathbf{S}_2-\mathbf{R}_2) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad =\dfrac{n_1-n_2}{2}(\mathbf{s}_1+\mathbf{s}_2).\end{array}\right\} \quad . \; . \; . \quad (38)$$

It is almost intuitive that the mean factor (n) should correspond to the mean vectors in the way that these equations confirm. The second and third are interpretable at sight in their last members as expressing colinear vectors parallel to the plane (ABC). Denote these respectively by $(2\mathbf{D}_1, 2\mathbf{D}_2)$; it is clear that a changed sign for (n_2) interchanges them. In terms thus chosen, it follows that

$$\left.\begin{array}{l}\mathbf{S}_1(-\mathbf{D}_1+\mathbf{D}_2)=\mathbf{R}_2+(\mathbf{D}_1+\mathbf{D}_2)\,; \;\; \mathbf{S}_2+(\mathbf{D}_1-\mathbf{D}_2)=\mathbf{R}_1-(\mathbf{D}_1-\mathbf{D}_2)\,; \\ \qquad (\mathbf{S}_2-\mathbf{R}_2-2\mathbf{D}_2)+(\mathbf{S}_1-\mathbf{R}_1-2\mathbf{D}_2)=0\,; \\ \qquad (\mathbf{S}_2+\mathbf{R}_2+2\mathbf{D}_1)-(\mathbf{S}_1+\mathbf{R}_1-2\mathbf{D}_1)=0.\end{array}\right\} \quad . \; . \; . \quad (39)$$

If next the extra condition be attached that $(\mathbf{s}_1-\mathbf{s}_2)$ shall be perpendicular to $(\mathbf{s})$, the symmetries of equations (39), in comparison with those of equations (29, 30, 31), make correspondence permissible of $(\mathbf{M})$, either with $(2\mathbf{D}_1)$ or with $(2\mathbf{D}_2)$, according to the actual occurrence of the positive sign for the scale-factors. In this scheme, equation (35) is easy to locate as a special combination; and equation (19) finds its place. The last of equations (39) bring to light the well-known "symmetrical average function." The important part played in all these developments by the mean factor (n) must be explicitly recognized. That is intimately associated with its necessary (automatic) appearance in ($n\rho_1, n\rho_1'$); it is one main connecting link between the original vectors and those obtained by inversion (crossed pairing). The perpendicularity of (**M**, **s**), requiring equal orthogonal projections upon the line of (**s**) for the *vectors* ($\mathbf{Q}_2$, $\mathbf{Q}_2''$), considered by itself demands no more than equality of scale-factors applied to the same segment of that line. The consideration that here precedes makes the selection (n**s**) natural.

The material of this particular discussion traverses familiar ground, so far as the final facts about conjugate vectors are concerned. But the line of attack there formulated is capable of deducing novel results elsewhere.

University of California.

LXIV. *Contact Difference of Potential and Thermionic Emission.* By O. W. Richardson, *F.R.S., Wheatstone Professor of Physics, and* F. S. Robertson, *M.I.E.E., Lecturer in Electrical Engineering, University of London, King's College* *.

It has been pointed out by one of us † that the following relation should subsist between the contact potential difference V between two surfaces at the absolute temperature T and their thermionic electron saturation currents i_1, i_2 per unit area at the same temperature:—

$$V = \frac{kT}{e}\log\frac{i_2}{i_1}. \qquad (1)$$

In this equation, k is Boltzmann's constant and e the electronic charge.

Observations which confirm the validity of this equation, approximately at any rate, have been made by us in the course of some experiments with a thoriated tungsten filament. The filament was of tungsten containing 1 per cent. of thorium and was kindly supplied to us by the Tungsten Manufacturing Co. Ltd., 231 Strand, London. It was 3·0 cm. long and 0·100 mm. in diameter, and was mounted axially in a cylindrical glass tube and surrounded by a coaxal copper anode. The general arrangements for evacuation and for controlling the temperature of the filament, etc., were similar to those described in our paper on the effect of gases on the contact difference of potential between metals ‡. After baking out

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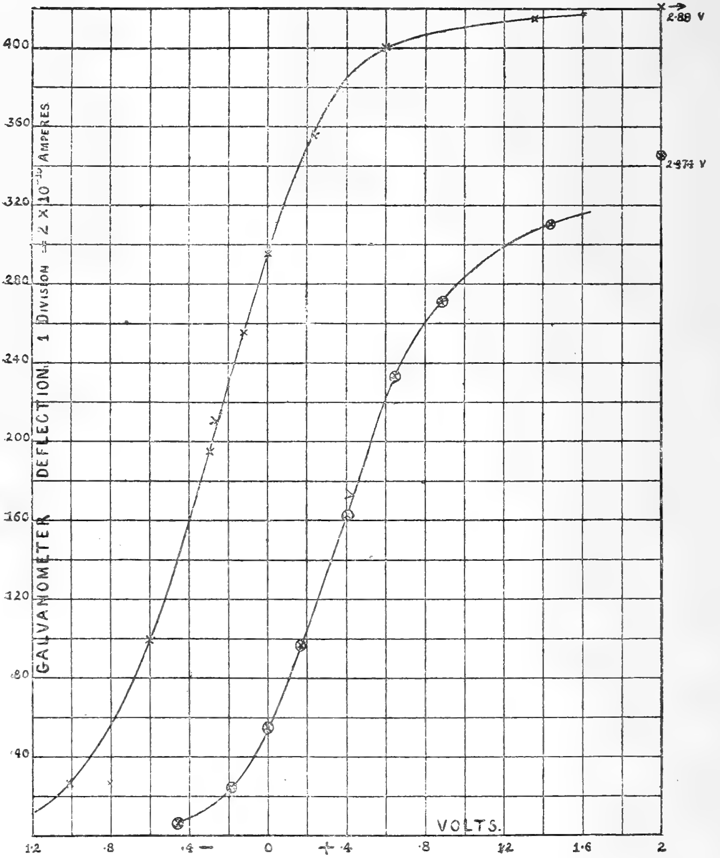
* Communicated by the Authors.

† O. W. Richardson, Phil. Mag. vol. xxiii. p. 265 (1912); and 'Emission of Electricity from Hot Bodies,' p. 41. Second Edition (1916).

‡ Phil. Mag. vol. xliii. p. 162 (1922).

the tube, exhausting with the mercury-vapour pump, etc., and heating the filament for some hours, it was found to have a fairly stable characteristic curve in the neighbourhood of that to the left-hand side of fig. 1. Later on, the emission was found to have risen to an enormously higher value, and was right outside the scale of the available measuring instruments with the same temperature as indicated by the resistance of the filament. The emission was now lowered by reducing the filament temperature to a value comparable with that ruling before the change occurred, and the characteristic was now found to be stable in the neighbourhood of the right-hand curve in fig. 1. This displacement of the characteristic

Fig. 1.



corresponds to a change of 0·71 volt in the potential difference between cathode and anode, and is in such a direction as to indicate that the filament had suddenly become relatively more electropositive to that extent.

There seems no reason to doubt that most of this change in the contact potential occurred at the heated filament. Assuming that the whole change is at the filament, these observations furnish the material for an approximate test of equation (1). The test is only approximate in any event because it was not possible to ascertain the temperature of the filament with accuracy. When its inverse resistance was 0·521 ohm^{-1}, corresponding to the left-hand curve in fig. 1, its temperature was estimated with a Cambridge & Paul Optical Pyrometer at 1583° K. Another estimate can be obtained if we assume that it was giving the pure tungsten emission at this stage. Using K. K. Smith's tungsten data we calculate T=1450° K; and using Langmuir's T=1507° K for this limit, the average of these three estimates is 1480° K.

The emission for a resistance of $(\cdot521)^{-1}$ after the rise was too large for us to measure with our instruments, but was obtained by extrapolation. It was found that the currents at various values of the inverse resistance were as follows :—

$i_2(1=2\cdot06\times10^{-10}$ amp.)......	10·2	21·0	45	91·5	165	318
$\log_{10} i_2$	1·01	1·323	1·653	1·962	2·218	2·503
$R^{-1}(\text{ohm}^{-1})$	·774	·764	·740	·726	·714	·698

The relation between the logarithm of this current and R^{-1} is found to be linear, and from the plot it appears that the value of $\log_{10} i_2$ for $1/R=\cdot521$ is 5·96. The value of $\log_{10} i_1$ for $1/R=\cdot521$ was 2·62. Substituting the known values of k and e and the experimental value of T, viz. 1480° K, and inserting the factors for volts and natural logarithms, it appears that these data give V=0·96 volt as compared with the measured value 0·71 volt.

This is probably as substantial an agreement as could be expected, considering the uncertainty of some of the data. We are engaged in further experiments which it is believed will eliminate these elements of uncertainty. The difficulties, however, are not inconsiderable, and it is clear that some time must elapse before further results of value are obtained.

A reference to these experiments was made by one of us in his Presidential Address to Section A of the British Association at the Edinburgh meeting, 9th September 1921.

LXV. *On the Deformation of the "Rings and Brushes" as observed through a Spath Hemitrope.* *By* B. N. Chuckerbutti, *M.Sc., Assistant Professor of Physics, Calcutta University*[*].

[Plate IX.]

1. *Introduction.*

CRYSTALS are frequently found which are obviously of a composite character, that is, are composed of more than a single individual crystal of the same substance and in which the parts belonging to different individuals are united in a definite and regular manner, the peculiar mode of union being characteristic of the substance. The true nature of the composite structure is often betrayed by the presence of *re-entrant angles*, forming notches (as in Diamond crystals), arrow-head shapes (as in Gypsum), knee-shapes (as in Cassiterite), cruciform (as in Staurolite), or heart-shapes (as in Fluorspar); but not infrequently the two or more individuals are so intimately blended, that the appearance at first sight is that of a single individual crystal.

The law defining the manner in which the composition occurs is usually stated as follows:—

The two individuals are first supposed to be arranged parallel to each other, with one face of each in mutual contact, and then in order to produce the twin, one individual is supposed to be rotated to 180°, upon a plane, which is called the *twin-plane*, and about the normal to the plane as axis, which is called the *twin-axis*. But it is necessary to point out here, that in the actual process of the formation of the twins, no such two different crystals are brought into contact and then one turned through 180°, as stated above. The orientation takes place amongst the crystalline molecules of their own accord during the process of formation. Hence, the *twin-plane* is not necessarily always the plane of contact. In general, the plane of twinning may be any actual or possible face, except obviously a plane of symmetry of the crystal.

The twinning may be either of Primary or of Secondary origin. The former refers to the case when the formation takes place of itself without the intervention of some external agency during the process; but when the twinning takes place subsequently to the original formation of

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[*] Communicated by the Author.

the crystal or crystalline mass, by means of external pressure, it is called secondary. Closely related to the cleavage-direction in their connexion with the cohesion of the molecules of a crystal, are the *Gliding planes* (Gr. Gleitflächen) or directions parallel to which a slipping of the molecules may take place under the application of an external force. This molecular slipping may be attended by a rotation through 180° of the molecules and the resulting twin formed.

According to the mineralogists, Iceland-spar belongs to a class of crystals which always produce twinning lamellæ, that is, one twinning plane in the case of this crystal is always followed by another at a very short distance so that a thin layer of similarly oriented molecules is formed. These are found abundantly in nature and, moreover, the pressure upon the cleavage-fragment of Iceland-spar results in the formation of a number of thin laminæ in twinning position to the parent mass. Secondary twinning lamellæ are often observed in natural cleavage masses of calcite.

The explanation of the mechanism of formation of twin crystals is rather difficult. Lord Kelvin*, however, has touched upon the problem. He has given a very lucid exposition of the whole process of crystal-building from a solution. In the particular class of crystals producing twins, he considers the constituent molecules symmetrical on the two sides of a plane passing through itself and also on the two sides of a plane perpendicular to this plane, that is to say, his crystalline molecules are egg-shaped. A real crystal which is growing by addition to a face would give layer after layer regularly. But, if *by some change in internal circumstances*, the molecules that would go to the formation of a layer are all oriented to 180° with respect to the molecules that formed the previous layer, a twinning plane is formed, and if the remaining layers form in the same way as the last mentioned one, then we shall get a crystal having two different parts separated by a twin-plane between. If, again, the process of orientation continues only to some layers and then, due to *the re-establishment of the initial conditions*, the layers form as at the start, we shall get two portions to the two sides with similarly oriented molecules, enclosing a thin layer in which the molecules are turned through 180°. The case will resemble that of Iceland-spar. But the main difficulty in the explanation is to understand *what is that change in the circumstances* that causes the crystalline molecules to turn through 180° in the process of

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* Baltimore Lectures, p. 629, Art. 37–39.

crystal formation, and how is it in the case of Iceland-spar that *the initial conditions are re-established* after a thin layer is formed under the changed conditions. The difficulty is still greater when we come to consider the case of repeated twinning as in the case of potassium chlorate crystals, where it is found that a very large number of twinning layers may be formed with a most surprisingly regular periodicity and constancy of thickness. Thus there is a good deal in regard to the mechanism of formation of these twinning layers that is as yet but imperfectly understood.

2. *Optical behaviour of a Spath Hemitrope.*

On looking at a source of light through a twin crystal of Iceland-spar, generally it is found that three images of the source are formed, the central one of which is always stationary. If the source of light is an incandescent electric lamp, then the images are beautifully coloured, the nature of the colour changing with the orientation of the plane of the crystal to the incident beam. It is also observed that the two outside images are polarized in perpendicular planes. On rotating the crystal, the two outside images are found to rotate about the central one, and in the course of a revolution there are positions in which both of them disappear, the remaining one becoming the most brilliant for the time.

The author has also found that when a beam of light is allowed to fall upon a crystal cut perpendicular to the axis and also polished in such a way that the lines, in which the twinning lamina cuts the planes of the main crystal, are on the surface, some interesting diffraction effects are observed. Fringes are noticed in the region of the transmitted light which show a remarkable asymmetry. The edges of the lamina also appear to be luminous. The phenomena appear to belong to the class of laminar diffraction effects, but there are certain features regarding them of which the explanation is not clear. The author is at present engaged in a fuller study of these effects, and the investigation mentioned above will probably prove of considerable interest in relation to the determination of the optical nature of the twinning layer.

On examining the crystal with convergent plane polarized light and between crossed nicols, the ordinary "rings and brushes" are found to be distorted, the amount and the nature of the distortion changing with the orientation of the crystal. However, in some cases, the distortion more or less resembles that produced by the superposition of a quarter-wave mica-plate upon a crystal of Iceland-spar cut perpendicular to the axis, so that the plane containing the optic axes of the mica-plate makes an angle of 45° with the vibration planes of the crossed nicols.

The explanation of the phenomena of refraction has been given in text-books on Optics *. There, the formation of the three images and the polarization are all explained. The disappearance of the outside images in certain positions, as stated before, is connected with the orientation of the optic axis of the intervening layer to that of the main crystal.

The problem of the form of the rings and brushes through a twin crystal has been treated mathematically, but the case has always been considered where a twinning plane separates two crystals. The problem of the two similar crystal wedges separated by a thin twinned lamina inserted between them in an inclined position appears not to have been solved, and an investigation in this direction forms the subject-matter of the present paper.

3. *Explanation of the Photographs.*

The crystal that was employed in the following experiments was cut perpendicular to the axis, and the portions free from the twinning layer showed the ordinary "rings and brushes" peculiar to crystals cut in such a manner. The angle which the twinning plane makes with the faces of the crystal is determined by observing the marginal outline of the plane as seen on looking through the edge of the crystal.

The Hemitrope, as examined with tourmaline tongs, shows very beautiful distortions and changes in the usual circular ring-system. It is difficult to photograph the successive stages completely, and it is found that the changes repeat themselves four times during a turn of the crystal through 2π, when the tourmalines are crossed,—the position for which most of the observations were made. The rings lose their circular nature altogether, and they will be found to be elliptic as if pressed up and down or sideways. Moreover, the change due to the introduction of the thin twin plane is most prominent near the central part of the system. These changes at the centre mixing up with the crosses make the central portion look rather cumbrous.

Figs. 1 to 4 (Pl. IX.) represent the changes for a rotation of the crystal through $\pi/2$, when the analyser has its

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* Mascart, *Traité d'Optique*, vol. ii. p. 192.

plane of polarization vertical and the polarizer horizontal. In fig. 1 the crystal is placed so that the twinning layer extends vertically up and down, inclined in such a manner that its sections with the faces of the crystal are vertical straight lines. Light is always allowed to fall *normally* upon the first face of the crystal, as otherwise the three images of which mention has been made before will make the system more complicated. Figs. 2, 3, 4 are obtained by rotating the crystal to the left in its own plane till the rotation amounts to $\pi/2$, when the system corresponds with fig. 1 but rotated through 90°. As we proceed further beyond $\pi/2$, the figures 2, 3, 4 come in the reverse order, fig. 4 being followed by figs. 3 and 2 and at π we get back to fig. 1. On rotating further, figs. 2, 3, 4 come in turn, similarly as in the first quadrant, and the figure at $3\pi/2$ corresponds with the one at $\pi/2$. The order of succession of the system along the last quadrant corresponds with that of the second quadrant. Figs. 5 to 8 were obtained by rotating the tourmalines in some position other than the crossed and at the same time rotating the crystal also. In general, the systems are rather cumbrous in these cases and the four cases are selected out, as showing the changes rather systematically. Figs. 7 and 8 have the peculiarity that they are complementary in nature to figs. 4 and 1 respectively, although they were obtained when the tourmaline planes were not parallel but inclined at an angle of about 45°.

4. *Physical Theory.*

In general, if δ be the path retardation of two rays due to their passage through a uniaxal crystal the equation to the generating curve to the isochromatic surface is

$$\{(\mu_0^2-\mu_e^2)y^2+\delta^2\}^2=4\mu_0^2\delta^2(x^2+y^2),$$

where the optic axis lies along the axis of X.

In case of a regular crystal of thickness T, the section of the isochromatic surface by a plane $x=\mathrm{T}$ gives the equation for the rings, and the points giving the same path-retardation are equidistant from the centre of the system. Now the interposition of the thin layer which again has its optic axis inclined to the optic axis of the main crystal, causes different path-retardation upon the interfering rays, so that the points of equal path-retardation are not equidistant from the centre, and as a result we should expect distorted curves.

Let

$$l\xi + m\eta + n_1\zeta = 1,$$

$$l\xi + m\eta + n_2\zeta = 1,$$

be the equations of the two waves in unit time after passing through a point o of the surface of the crystal.

[n_1 and n_2 are the reciprocals of the intercepts made on the normal (axis ζ) to the plate through the point o by the refracted waves in unit time after passing through o.]

If θ be the azimuth of the plane of incidence with respect to that of $\xi\zeta$ and v be the velocity of light in air, then

$$l = \frac{\sin i \,.\, \cos\theta}{v}, \qquad m = \frac{\sin i \,.\, \sin\theta}{v},$$

where i=angle of incidence.

Suppose, that the plane $\xi\zeta$ contains the greatest axis oz of the ellipsoid of polarization, the plate being on the positive side of ζ, then if ox, oy, oz be the axes of the ellipsoid and $zo\zeta = \chi$, we get by transformation from the axes of optical symmetry to the new axes,

$$x = \xi\cos\phi\cos\chi - \eta\sin\phi + \zeta\cos\phi\sin\chi,$$

$$y = \xi\sin\phi\cos\chi - \eta\cos\phi + \zeta\sin\phi\sin\chi,$$

$$z = -\xi\sin\chi + \zeta\cos\chi.$$

The equation to the wave surface, referred to the axes of optical symmetry is

$$\frac{a^2x^2}{\sigma^2 - a^2} + \frac{b^2y^2}{\sigma^2 - b^2} + \frac{c^2z^2}{\sigma^2 - c^2}.$$

From the condition that the plane $l\xi + m\eta + n\zeta = 1$ should touch the wave surface in the new system of coordinates, we find

$$\frac{\delta}{\mathrm{T}} = -\frac{\sqrt{v^2 - a^2\sin^2 i}}{a} + \frac{(a^2 - c^2)\sin\chi\cos\chi\cos\theta\sin i}{a^2\cos^2\chi + c^2\sin^2\chi}$$

$$+ \frac{\sqrt{(a^2\cos^2\chi + c^2\sin^2\chi)(v^2 - c^2\sin^2 i) - c^2(a^2 - c^2)\sin^2\chi \,.\, \cos^2\theta \,.\, \sin^2 i},}{a^2\cos^2\chi + c^2\sin^2\chi}$$

where $\qquad \delta = v\mathrm{T}(n_2 - n_1).$

Hence, for a crystal cut perpendicular to the axis ($\chi = 0$),

$$\therefore \quad \frac{\delta}{\mathrm{T}} = \left\{ \sqrt{v^2 - c^2\sin^2 i} - \sqrt{v^2 - a^2\sin^2 i} \right\} / a.$$

Let T, t be the thicknesses of the main crystal, and of the thin twin layer respectively, and δ_1 and δ_2 be the corresponding path retardations. In the present case, if we assume that the twin layer is also cut perpendicular to the optic axis, then from the angle (30°) at which its plane cuts the faces of the crystal, we must have $\chi=60°$ for the thin layer. So that the expression for the retardation in terms of the refractive indices takes the form,

$$\frac{\delta_2}{t}=\sqrt{\mu_e^2-\sin^2 i}+\frac{\mu_0^2-\mu_e^2}{\mu_0^2-3\mu_e^2}\cdot\sqrt{3}\,.\sin i\,.\cos\theta$$

$$-\frac{\sqrt{\dfrac{\mu_0^2-3\mu_e^2-4\mu_0\sin^2 i\cos^2\theta}{\mu_e}}}{2\mu_0(\mu_0^2+3\mu_e^2)}.$$

For the rays which fall normally upon the face of the crystal (*i. e.*, the rays which make an angle of 30° with the normal to the twin layer),

$$\delta_2=t\{1{\cdot}3186+0{\cdot}05\cos\theta+{\cdot}0028\cos^2\theta\}$$

and $\qquad \delta_1=\mathrm{T}\mu_0\{\mu_0-\mu_e\}.$

Moreover,

$$\delta_1=\mathrm{T}\mu_0\left\{\frac{(\mu_0^2-i_1^2)^{\frac{1}{2}}}{\mu_0}-\frac{(\mu_e^2-i_1^2)^{\frac{1}{2}}}{\mu_e}\right\},$$

where i_1 = angle of incidence (very small).

The thickness of the twin layer as seen under a high power microscope and estimated with the help of a micrometer eyepiece is about 2λ. So that

$$\delta_2=2\lambda(1{\cdot}3186+0{\cdot}05\cos\theta+0{\cdot}0028\cos^2\theta).$$

Now as the azimuth angle increases from 0° to 90° the value of δ_2 diminishes. On the other hand, δ_1 goes on increasing as the angle of incidence is increased, and is constant for the same angle of incidence.

If r be the radius-vector of the interference minima or maxima, then we may put

$$r^2=k(\delta_1+\delta_2,)$$

where k is a constant. Hence we can expect the elliptic form of the curves, the radius-vector for an azimuth of 90° being the least. Moreover, at a distance from the centre where i is great, δ_1 will be very great in comparison to δ_2, which latter may then be safely neglected, the radius-vector in those cases being given by $r^2=k\delta_1$.

Another important feature of this thin twin plane is the asymmetric laminary diffraction* pattern to be observed near the two edges of the twin plane, with a beam of light incident normally upon the surface of the crystal. This problem, however, is under investigation.

The experimental work described in this paper was carried out in the Palit Laboratory of Physics and the writer wishes to express his thanks to Prof. C. V. Raman for kindly providing all facilities for work.

University College of Science, Calcutta.
24th August, 1921.

LXVI. *Coupled Vibrations by means of a Double Pendulum.*

By A. L. NARAYAN, *M.A.*†

[Plates X. & XI.]

FOR the production of high-frequency oscillations required in radio-telegraphy, one of the most important elements in the oscillation circuit is the oscillation-transformer, which is simply a magnetically-coupled oscillating circuit possessing a primary and a secondary each containing inductance and capacity in series. In order to elucidate and interpret the theory of these electric circuits and illustrate how, when oscillations are excited in one circuit, these two circuits act and react on each other so that the result is that oscillations of two different periods are set up in both circuits, one greater than and the other less than the natural period of either circuit taken separately, mechanical systems were described by Prof. Thomas Lyle, Phil. Mag. vol. xxv. pp. 567–572 (April 1913): Prof. Barton and Miss Browning, Phil. Mag. vol. xxxiv. p. 246 (1917), vol. xxxv. p. 62 (1918), and vol. xxxvi. p. 36 of the same year; and Mr. Jackson, Phil. Mag. March and September 1920.

In this paper the author describes an entirely different kind of mechanical system, which gives results very similar to those obtained by Prof. Barton and Miss Browning, and Mr. Jackson, in the papers referred to above. At the same time, the whole arrangement is more neat and much simpler than the very elaborate one adopted by Mr. Jackson, and the method of photographing the vibrations in the present case is essentially different from that of the previous authors.

The coupled system treated in these pages consists, as shown in the two diagrams (Pl. X.), of two rigid pendulums A and B,

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* P. N. Ghosh, Proc. Roy. Soc. A, vol. xcvi. (1919).

† Communicated by the Author.

of which A consists of a steel rod furnished with a heavy bob which can be screwed at different points so as to vary the moment of inertia of the system, and it can turn freely about a horizontal axis by means of a knife-edge which can be fixed at different points—thus varying the point of suspension also. Similarly the pendulum B consists of a steel rod and a heavy bob, and it is suspended from A by means of a highly polished steel knife-edge resting in a V-groove of a small steel bracket which can be screwed at different points along the length of A. Thus the degree of coupling can be varied at will.

The paper includes twenty photographic traces of the motion of the pendulums under various conditions. The method adopted in this case for photographing the vibrations is wholly different from that adopted by Prof. Barton and Miss Browning and Mr. Jackson in their various experiments on coupled oscillations. Each of the pendulums A and B carries (as can be clearly seen from the second photograph) a small galvanometer mirror of about 1 m. radius, with its plane perpendicular to that of the vibration of the pendulum, and the mirror can be turned (by means of a simple mechanism) about a horizontal and a vertical axis, for final adjustment to get the two reflected spots exactly one above the other on the slit of the camera. When the pendulum vibrates, the mirror mounted on it rotates about the axis of rotation of the pendulum. A beam of light proceeding from a pinhole is projected on to the mirror, and the reflected spot moves up and down, when the pendulum vibrates; and the two spots formed by reflexion from the mirrors are made to fall on a narrow vertical slit of a moving plate camera, the plate inside which is moved at a uniform speed by means of a chronograph, as shown in the photograph of the apparatus. Throughout this work Ilford Empress Plates are used and are developed in a normal solution of metol-hydroquinone.

Theory of the Double Pendulum. Equation of Coupling.

The annexed figure represents the projection on a vertical plane perpendicular to the axis of rotation.

Let m_1 and m_2 be the masses of the two pendulums A and B;

G_1 and G_2, their mass centres;

O_1 and O_2, their axes of rotation;

K_1 and K_2, radii of gyration of (i.) A about O and (ii.) of B about G_2 respectively;

and $O_1G_1 = h_1$; $O_2G_2 = h_2$; $O_1O_2 = a$;

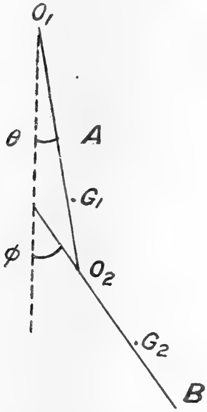
θ and ϕ the inclinations of O_1G_1 and O_2G_2 to the vertical.

Then, if T represents the K E. of the whole system,

$$2T = m_1K_1^2\dot{\theta}^2 + m_2K_2^2\dot{\phi}^2 + \left(m_2h_2^2\dot{\phi}^2 + m_2a^2\dot{\theta}^2 + 2m_2ah_2\dot{\theta}\dot{\phi}\cos(\phi-\theta)\right);$$

and if W = work done on the system,

$$W = -m_1gh_1\cos\theta - m_2g(a\cos\theta + h_2\cos\phi) + C.$$



Since there are no extraneous forces acting on the system, equations of motion of the system are given by:

$$\frac{d}{dt}\cdot\frac{\partial T}{\partial\dot{\theta}} - \frac{\partial T}{\partial\theta} = -\frac{\partial W}{\partial\theta},$$

$$\frac{d}{dt}\cdot\frac{\partial T}{\partial\dot{\phi}} - \frac{\partial T}{\partial\phi} = -\frac{\partial W}{\partial\phi}.$$

Thus for small oscillations we have:

$$(m_1K_1^2 + m_2a^2)\ddot{\theta} + (m_1h_1 + m_2a)g\theta + m_2ah_2\ddot{\phi} = 0, \quad . \quad (1)$$

$$ah_2\ddot{\theta} + gh_2\phi + (K_2^2 + h_2^2)\ddot{\phi} = 0. \quad . \quad (2)$$

By analogy with the electrical problem, we can write for the coefficient of coupling between the two circuits,

$$\gamma^2 = \frac{m_2a^2h_2^2}{(m_1K_1^2 + m_2a^2)(K_2^2 + h_2^2)}.$$

To solve these equations, assume:

$$\theta = A_1\cos(nt+\alpha) \quad \text{and} \quad \phi = B_1\cos(nt+\alpha).$$

$$\therefore \quad \ddot{\theta} = -n^2A_1\cos(nt+\alpha)$$

$$\text{and} \quad \ddot{\phi} = -n^2B_1\cos(nt+\alpha).$$

Substituting these values in (1) and (2) above, we have

$$A_1\{(m_1K_1^2+m_2a^2)n^2-(m_1h_1+m_2a)g\}+B_1m_2ah_2n^2=0, \quad . \; . \; . \quad (3)$$

and

$$A_1ah_2n^2+B_1\{(K_2^2+h_2^2)n^2-gh_2\}=0. \quad . \; . \quad (4)$$

Eliminating the ratio $\frac{A_1}{B_1}$, we obtain the determinantal equation :

$$\begin{vmatrix} (m_1K_1^2+m_2a^2)n^2-(m_1h_1+m_2a)g\,; & m_2ah_2n^2\,; \\ ah_2n^2\,; & (K_2^2+h_2^2)n^2-gh_2 \end{vmatrix} = 0.$$

Put

$$(m_1K_1^2+m_2a^2)(K_2^2+h_2^2)=k,$$

$$h_2(m_1K_1^2+m_2a^2)+(K_2^2+h_2^2)(m_1h_1+m_2a)=b\,;$$

we can write down the above determinant as

$$n^4k(1-\gamma^2)-n^2gb+h_2g^2(m_1h_1+m_2a)=0. \quad . \; . \quad (5)$$

This is a quadratic equation in n^2, thus giving two admissible values of n^2.

The roots are given by

$$n^2=\frac{bg\pm\sqrt{b^2g^2-4h_2g^2(m_1h_1+m_2a)(1-\gamma^2)k}}{2k(1-\gamma^2)}.$$

Calling the two roots p^2 and q^2, we have

$$\frac{p}{q}=\left\{\frac{b+\sqrt{b^2-4h_2k(m_1h_1+m_2a)(1-\gamma^2)}}{b-\sqrt{b^2-4h_2k(m_1h_1+m_2a)(1-\gamma^2)}}\right\}^{\frac{1}{2}}. \quad . \; . \quad (6)$$

Therefore the complete solution is

$$\theta=A_1\cos(pt+\alpha)+A_2\cos(qt+\beta), \quad . \; . \; . \; . \quad (7)$$

$$\phi=B_1\cos(pt+\alpha)+B_2\cos(qt+\beta), \quad . \; . \; . \; . \quad (8)$$

where p and q depend upon the constitution of the system, and A_1, A_2, B_1, B_2, and α and β are arbitrary and enable us to satisfy any prescribed initial conditions.

Thus the two pendulums act and react on each other, creating in each a motion which is made up of two superposed S.H. vibrations of different periods. The difference between the two frequencies depends upon the coefficient of coupling (γ) of the circuits. As in the case of the electrical problem, if γ is a small fraction the circuits may be said to be loosely coupled, and when γ is large, they may be said to be closely coupled. When the coupling is loose and p and q are nearly equal, we have a vibration of nearly constant period but whose amplitude fluctuates between $A_1 \pm A_2$ and $B_1 \pm B_2$, thereby presenting the well-known phenomenon of beats.

The ratios $\frac{A_1}{B_1}$ and $\frac{A_2}{B_2}$ can be found most simply from equation (2) with the respective values of n^2 inserted. Thus we have

$$B_1 = \frac{ah_2p^2}{gh_2-(K_2^2+h_2^2)p^2} \cdot A_1, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$B_2 = \frac{ah_2q^2}{gh_2-(K_2^2+h_2^2)q^2} \cdot A_2. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

To obtain the special solution for any particular case, we must know the initial displacements and velocities and determine the four constants A, B, α, and β. As a preliminary to this, we can write

$$\theta = A_1 \cos(pt+\alpha) + A_2 \cos(qt+\beta), \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\left.\begin{aligned}\phi = &\frac{ah_2p^2}{gh_2-(K_2^2+h_2^2)p^2} \cdot A_1 \cos(pt+\alpha)\\ &+\frac{ah_2q^2}{gh_2-(K_2^2+h_2^2)q^2} \cdot A_2 \cos(qt+\beta),\end{aligned}\right\} \quad . \quad (12)$$

$$\dot{\theta} = -A_1p \sin(pt+\alpha) - A_2q \sin(qt+\beta), \quad . \quad . \quad . \quad . \quad (13)$$

$$\left.\begin{aligned}\dot{\phi} = &-\frac{ah_2p^2}{gh_2-(K_2^2+h_2^2)p^2} \cdot A_1p \sin(pt+\alpha)\\ &-\frac{ah_2q^2}{gh_2-(K_2^2+h_2^2)q^2} \cdot A_2q \sin(qt+\beta).\end{aligned}\right\} \quad . \quad (14)$$

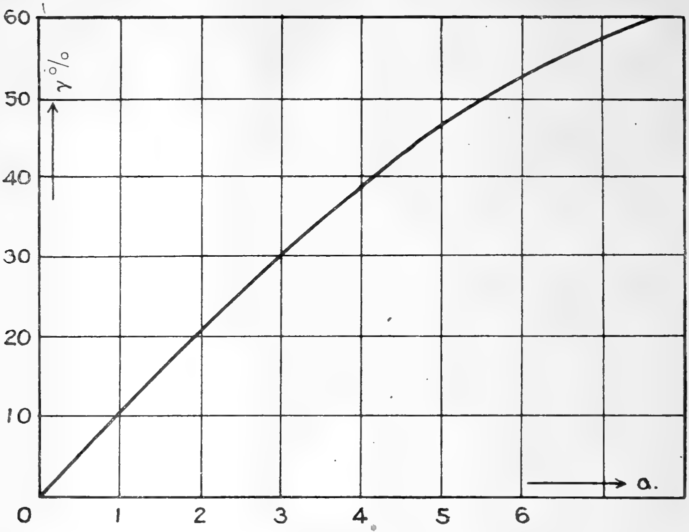
From these equations we can obtain the particular solution in any case from a knowledge of the initial conditions.

The values of γ and $\frac{p}{q}$ the ratio of the two superposed S.H. vibrations; and the relation between (i.) γ and α (ratio of the distance from the point of suspension of A to that of B) to the whole length of A, or rather the length of simple pendulum equivalent to A, and (ii.) γ and $\frac{p}{q}$, is represented in graphs (i.) and (ii.).

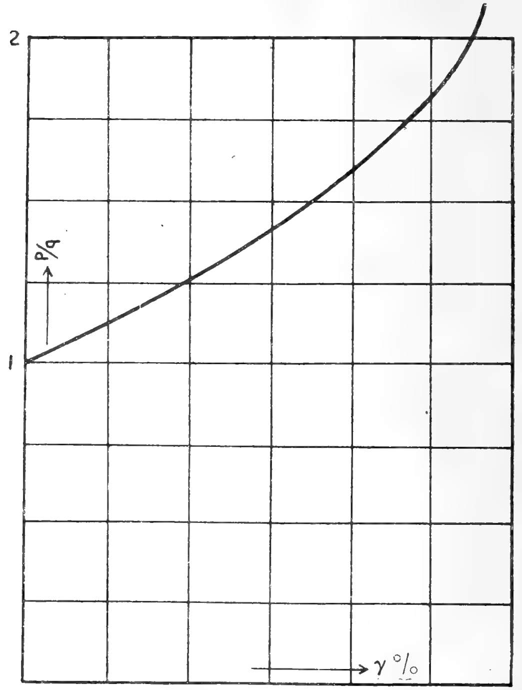
Graph (iii.) is given to show the relation between γ and $\frac{p}{q}$ in the electrical problem similar to the mechanical one in question.

An examination of graphs (ii.) and (iii.) and the photographic reproductions given in Plate XI. shows how in both cases (mechanical and electrical) the difference between the two superposed S.H.M.'s becomes greater and greater with the progressive increase of coupling.

Graph i.

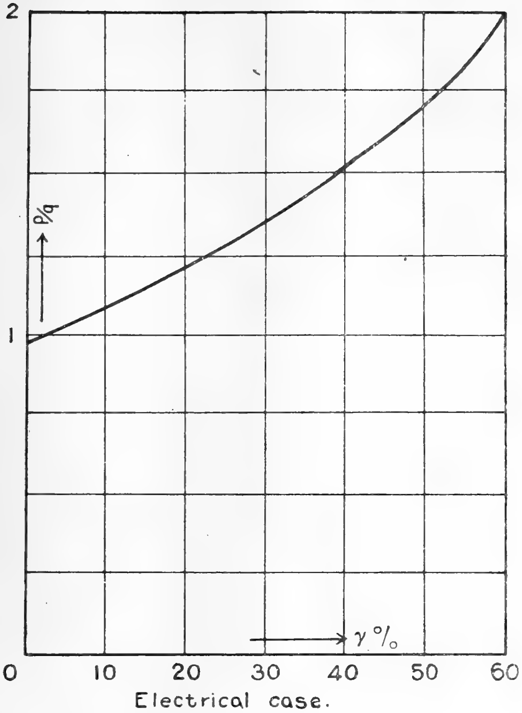


Graph ii.



Mechanical case.

Graph iii.



Values of γ; $\frac{p}{q}$; and α.

Serial No.	γ per cent.	$\frac{p}{q}$.	α.
1 …………	0	1	0
2 …………	5·3	1·06	·05
3 …………	10·6	1·129	·1
4 …………	15·7	1·193	·152
5 …………	19·8	1·260	·19
6 …………	24·7	1·313	·25
7 …………	30·5	1·393	·305
8 …………	34·6	1·464	·35
9 …………	42·6	1·601	·452
10 …………	49·5	1·757	·55
11 …………	52·8	1·860	·6

Figs. 1 to 20 (Pl. XI.) are reproductions of the photographs obtained with the above apparatus under various conditions; figs. 1 to 10 represent the oscillations of the system when the upper bob is displaced and the lower bob free, and figs. 10 to 20 represent those of the system when the lower bob is displaced and upper bob free. The figures clearly show the effect of progressively increasing the coupling; the first figures, in which the coupling is loose, show the phenomenon of beats.

Thus the coupled system treated above presents an exact mechanical analogy to the case of two mutually interacting electrical circuits; and at the same time it is much simpler, and therefore a more convenient model by which the properties of the electrical case can be demonstrated to a class or an audience. To a large audience it may be much better demonstrated by allowing the reflected spots of light to suffer another reflexion from a mirror rotating or oscillating about a vertical axis and then projecting the spots either on a screen or on a wall of the room.

With a modified form of apparatus, experiments have been carried out to illustrate the theory of three mutually interacting oscillating circuits, and the mathematical theory of the mechanical system "triple pendulum" is developed; and these results will be submitted for publication, shortly, in another paper.

Abstract.

The author, following Prof. Lyle, Prof. Barton and Miss Browning, and Mr. Jackson, describes an arrangement of mechanical systems as an exact analogy of two magnetically coupled circuits.

The mathematical theory of the system is developed; and the paper is accompanied by 20 photographic reproductions of the simultaneous traces of the two pendulums, the method adopted for photographing the vibrations being entirely different from that adopted by the previous writers.

At the same time, on account of its simplicity of arrangement it is a very convenient model by which the properties of electrical circuits can be easily demonstrated to a large class to satisfy the non-mathematical student, who is often mystified by the perfect silence of the high frequency circuits.

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25th April, 1921.

LXVII. *Mechanical Illustration of three Magnetically Coupled Oscillating Circuits.* *By* A. L. NARAYAN, *M.A.*[*]

[Plate XII.]

Synopsis.

THE paper is a continuation of the experiments made by the author on Coupled Circuits, and gives a short account of three mutually interacting pendulums which he used, in order to illustrate the theory of three magnetically coupled circuits. The mathematical theory of the mechanical system is developed.

The apparatus is a modified form of the one used by the author in his previous paper on Coupled Circuits. The paper is illustrated by ten photographic reproductions of the vibrations of the three pendulums under various conditions of starting, the method adopted for photographing the vibrations being essentially the same as that adopted by the author in his previous experiments, and therefore entirely different from that adopted by Prof. Barton and Miss Browning. The whole arrangement serves as a very convenient model for demonstrating the action of three electrical circuits to a large class.

In the Philosophical Magazine for November 1920, Prof. Barton and Miss Browning describe a model of triple pendulum as a mechanical analogue of three mutually interacting electrical circuits. In this paper an entirely different kind of mechanical system, which the author used in order to elucidate and interpret the theory of three magnetically coupled oscillating circuits, is described, and the mathematical theory of the mechanical system is developed.

The coupled system in this case is a modified form of one used by the author in his experiments to study variably coupled vibrations of two interacting circuits which illustrates the theory of the oscillation transformer. It consists (as shown in photograph fig. II., Pl. XII.) of three rigid pendulums, A, B, and C, of which A can turn freely about a horizontal axis by means of a steel knife-edge resting on a bracket. The pendulum B can be suspended from A by means of a steel knife-edge resting on a V-bracket, which can be screwed at different points along

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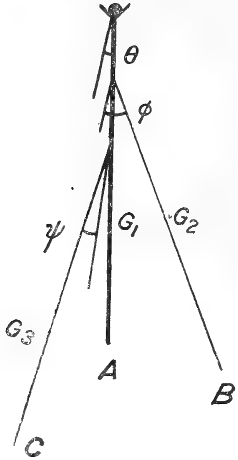
[*] Communicated by the Author.

the length of A so as to rotate about a parallel axis O′. Similarly, C is attached to A. Thus the degree of coupling between the various circuits can be varied at will.

It is worth noting that, at first, the three pendulums were connected as shown in photograph fig. I.; but subsequently as it was found that owing to want of symmetry in the load the pendulum A began to tilt slightly to one side as the coupling was increased, the arrangement shown in photograph fig. II. was adopted throughout. And it may be noted that there is essentially no difference between these two arrangements, as can be seen from the fact that in either case we get a cubic in n^2, thereby showing that the resultant motion in each case is composed of three superposed simple harmonic motions.

The paper includes ten photographic traces of the motion of the pendulums under various conditions, the method adopted for photographing these vibrations being exactly the same as that adopted by the author in his previous experiments. For a detailed description of this method, the reader is referred to his previous paper on coupled oscillations [*].

Equations of motion and coupling of the mechanical system.



The annexed figure represents a projection of the three pendulums on a vertical plane, perpendicular to the axes of rotation.

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[*] *Suprà*, p. 567.

Let : m_1, m_2, and m_3 the masses of the three pendulums ;

G_1, G_2, and G_3 the centres of gravity of the three pendulums ;

K_1 the radius of gyration of the pendulum A about the axis of rotation, and

K_2 and K_3 the radii of gyration of B and C about their centres of gravity ;

h_1, h_2, and h_3 the distances between the centres of gravity and the axes of rotation ;

a, b the distances of the points of suspension of B and C from that of A ;

and let the pendulums be inclined to the vertical at θ, ϕ, and ψ respectively.

In the case of a conservative dynamical system like this, where there are no extraneous forces, by Lagrange's equations we have for the equation of motion of three pendulums :

$$\frac{d}{dt}\cdot\frac{\partial T}{\partial \theta'}-\frac{\partial T}{\partial \theta}=-\frac{\partial V}{\partial \theta}, \quad . \quad . \quad . \quad \text{pendulum A}$$

$$\frac{d}{dt}\cdot\frac{\partial T}{\partial \phi'}-\frac{\partial T}{d \phi}=-\frac{\partial V}{\partial \phi}, \quad . \quad . \quad . \quad ,, \quad \text{B.}$$

$$\frac{d}{dt}\cdot\frac{\partial T}{\partial \psi'}-\frac{\partial T}{\partial \psi}=-\frac{\partial V}{\partial \psi}. \quad . \quad . \quad . \quad ,, \quad \text{C.}$$

Now the kinetic energy of the pendulum A about the axis of rotation is $\frac{1}{2}m_1K_1^2\left(\frac{d\theta}{dt}\right)^2$;

that of B relative to its centre of gravity is $\frac{1}{2}m_2K_2^2\left(\frac{d\phi}{dt}\right)^2$;

and hence the kinetic energy of B relatively to A is

$$\frac{1}{2}m_2K_2^2\left(\frac{d\phi}{dt}\right)^2+\frac{1}{2}m_2\left\{a^2\left(\frac{d\theta}{dt}\right)^2+h_2^2\left(\frac{d\phi}{dt}\right)^2\right.$$
$$\left.+2ah_2\frac{d\theta}{dt}\cdot\frac{d\phi}{dt}\,.\cos\overline{\phi-\theta}\right\}.$$

Similarly, kinetic energy of C relatively to A is

$$=\frac{1}{2}m_3K_3^2\left(\frac{d\psi}{at}\right)^2+\frac{1}{2}m_3\left\{b^2\left(\frac{d\theta}{dt}\right)^2+h_3^2\left(\frac{d\psi}{dt}\right)^2\right.$$
$$\left.+2bh_3\left(\frac{d\theta}{dt}\right)\cdot\left(\frac{d\psi}{dt}\right)\cdot\cos\overline{\psi-\theta}\right\}.$$

Therefore, if T represents the total kinetic energy of the system,

$$2T = m_1K_1^2\left(\frac{d\theta}{dt}\right)^2 + m_2K_2^2\left(\frac{d\phi}{dt}\right)^2 + m_3K_3^2\left(\frac{d\psi}{dt}\right)^2$$

$$+ m_2\left\{a^2\left(\frac{d\theta}{dt}\right)^2 + h_2^2\left(\frac{d\phi}{dt}\right)^2 + 2ah_2\frac{d\theta}{dt}\cdot\frac{d\phi}{dt}\,.\cos\overline{\phi-\theta}\right\}$$

$$+ m_3\left\{b^2\left(\frac{d\theta}{dt}\right)^2 + h_3^2\left(\frac{d\psi}{dt}\right)^2 + 2bh_3\frac{d\theta}{dt}\cdot\frac{d\psi}{dt}\,.\cos\overline{\psi-\phi}\right\},$$

and V the potential energy of the system (*i. e.* work done)

$$= (m_1h_1 + m_2a + m_3b)\,g\cos\theta + m_2gh_2\cos\phi + m_3gh_3\cos\psi$$
$$+ \text{K (a constant).}$$

∴ Equations of motion for small oscillations are :—

$$(m_1K_1^2 + m_2a^2 + m_3b^2)\frac{d^2\theta}{dt^2} + m_2ah_2\frac{d^2\phi}{dt^2} + m_3bh_3\frac{d^2\psi}{dt^2}$$
$$\doteq (m_1h_1 + m_2a + m_3b)\,g\theta, \quad . \quad (1)$$

$${}^*(m_2K_2^2)\frac{d^2\phi}{dt^2} + m_2ah_2\frac{d^2\theta}{dt^2} = m_2gh_2\phi, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$m_3K_3^2\frac{d^2\psi}{dt^2} + m_3bh_3\frac{d^2\theta}{dt^2} = m_3gh_3\psi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These equations show the analogy that exists between the mechanical case in question and the case of coupled electrical circuits, the equations of which we may write down as follows :—

$$L_1\frac{d^2q_1}{dt^2} + \frac{q_1}{s_1} = M_3\frac{d^2q_2}{dt^2} + M_2\frac{d^2q_3}{dt^2}, \quad . \quad . \quad . \quad . \quad (4)$$

$$L_2\frac{d^2q_2}{dt^2} + \frac{q_2}{s_2} = M_1\frac{d^2q_3}{dt^2} + M_3\frac{d^2q_1}{dt^2}, \quad . \quad . \quad . \quad . \quad (5)$$

$$L_3\frac{d^2q_3}{dt^2} + \frac{q_3}{s_3} = M_2\frac{d^2q_1}{dt^2} + M_1\frac{d^2q_2}{dt^2}, \quad . \quad . \quad . \quad . \quad (6)$$

where L's, q's, and M's have their usual significance.

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[*] The equations of motion of the first arrangement, namely that shown in photograph fig. I., will be of the form:

$$a_1\ddot{\theta} + b_1\ddot{\phi} + c_1\ddot{\psi} = d_1\theta,$$
$$a_2\ddot{\theta} + b_2\ddot{\phi} + c_2\ddot{\psi} = d_2\phi,$$
$$a_3\ddot{\theta} + b_3\ddot{\phi} + c_3\ddot{\psi} = d_3\psi.$$

The essential difference between these equations and those of the actual arrangement adopted finally being that the method of attachment of B and C to A in the second case reduces the coefficients c_2 and b_3 to zero.

By analogy from electrical practice, we can write down the coefficients of coupling as:

$$\frac{m_2{}^2a^2h_2{}^2}{\Sigma m_1\mathrm{K}_1{}^2 . m_2\mathrm{K}_2{}^2} \text{ between A and B,}$$

$$\frac{m_3{}^2b^2h_3{}^2}{\Sigma m_1\mathrm{K}_1{}^2 . m_3\mathrm{K}_3{}^2} \quad \text{,,} \quad \text{A and C,}$$

where

$$\Sigma m_1\mathrm{K}_1{}^2 = m_1\mathrm{K}_1{}^2 + m_2a^2 + m_3b^2,$$

and so on.

To solve the equations (1), (2), and (3), assume tentatively

$$\theta = \mathrm{A}\cos(nt+\epsilon),\ \phi = \mathrm{B}\cos(nt+\epsilon), \text{ and } \psi = \mathrm{C}\cos(nt+\epsilon).$$

Substituting these values in (1), (2), and (3), and eliminating θ, ϕ, and ψ, we have

$$\mathrm{A}\{\Sigma m_1\mathrm{K}_1{}^2 \times n^2 + \Sigma m_1h_1g\} + \mathrm{B}m_2ah_2n^2 + \mathrm{C}m_3bh_3n^2 = 0, \quad . \quad . \quad (7)$$

$$\mathrm{A}m_2ah_2n^2 + \mathrm{B}(m_2\mathrm{K}_2{}^2n^2 + m_2gh_2) = 0. \quad , \quad . \quad (8)$$

and

$$\mathrm{A}m_3bh_3n^2 + \mathrm{C}(m_3\mathrm{K}_3{}^2n^2 + m_3gh_3) = 0. \quad . \quad . \quad (9)$$

From this we get the determinantal equation:

$$\left|\begin{array}{ccccc} (n^2\Sigma m_1\mathrm{K}_1{}^2 + g\Sigma m_1h_1) & : & n^2m_2ah_2 & : & n^2m_3bh_3 \\ n^2m_2ah_2 & : & (n^2m_2\mathrm{K}_2{}^2 + m_2gh_2) & : & 0 \\ n^2m_3bh_3 & : & 0 & : & (n^2m_3\mathrm{K}_3{}^2 + m_3gh_3) \end{array}\right| = 0. \quad . \quad . \quad . \quad . \quad (10)$$

On simplification this gives us a cubic in n^2 of the form

$$a_1n^6 + b_1n^4 + c_1n^2 + d_1 = 0,$$

having three real positive roots.

Assuming that n_1, n_2, and n_3 are the three roots of this cubic equation, the most general solution would be

$$\theta = \mathrm{A}_1\cos(n_1t+\epsilon_1) + \mathrm{A}_2\cos(n_2t+\epsilon_2) + \mathrm{A}_3\cos(n_3t+\epsilon_3),$$

$$\phi = \mathrm{B}_1\cos(n_1t+\epsilon_1) + \mathrm{B}_2\cos(n_2t+\epsilon_2) + \mathrm{B}_3\cos(n_3t+\epsilon_3),$$

and

$$\psi = \mathrm{C}_1\cos(n_1t+\epsilon_1) + \mathrm{C}_2\cos(n_2t+\epsilon_2) + \mathrm{C}_3\cos(n_3t+\epsilon_3),$$

where n_1, n_2, and n_3 depend upon the constitution of the system, and A, B, C, and ϵ are arbitrary quantities and enable us to satisfy any prescribed initial conditions. Thus the three pendulums act and react upon one another, thereby creating in each a motion which is made up of three superposed S.H.M.'s of different periods. Thus, in accordance with the general principle, there are as many normal modes of vibration as there are degrees of freedom in the system. Photographic reproductions of the vibrations of the three pendulums under different conditions are given in Pl. XII. figs. 1–10. These curves show clearly that there are more than two simple harmonic vibrations in each.

With a modified form of apparatus, experiments are being carried on to illustrate the theory of combinational tones and their objective existence, showing thereby that when two simple harmonic forces of small but finite amplitude and of frequencies N_1 and N_2 are imposed on a vibrating system, there are generated in the system simple harmonic vibrations of frequencies $2N_1$, $2N_2$, N_1+N_2, and N_1-N_2 besides N_1 and N_2, the results of which will be published in a separate paper.

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LXVIII. *The Deflexion of a Ray of Light in the Solar Gravitational Field.* *By* Francis D. Murnaghan, *M.A., Ph.D., Assoc. Prof. of Applied Math., Johns Hopkins University* [*].

PROBABLY the most important experimental test of the General Relativity Theory is that dealing with the deflexion of a light-ray in its passage near the Sun. It is essential, therefore, that the mathematical discussion of the amount of deflexion to be expected should be clear, and should avoid all unnecessary assumptions. The treatment given in Eddington's classical and excellent Report [†] does not seem to meet these requirements, since it is somewhat indirect and appeals to theorems of optics which are proven in the text-books for Euclidean space alone; whilst it is the essence of the Relativity Theory that the space surrounding the sun is non-Euclidean. It is hoped that the following treatment will appeal to the reader as at once direct and not unnecessarily difficult.

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[*] Communicated by the Author.

[†] The Physical Society of London. 'Report on the Relativity Theory of Gravitation,' 2nd ed. (1920).

§ 1. *The minimal Geodesics or Light-Rays of a Gravitational Space : the Fermat-Huygens Principle of Least Time.*

The metrical geometry of the Space-Time continuum being characterized by

$$(ds)^2 \equiv g_{mn} dx_m dx_n$$

(m, n dummy or umbral symbols),

it is postulated that along a ray of light $(ds)^2=0$. Further, by (ds) is understood the positive square root of the expression for $(ds)^2$, so that the arc-length integral $\mathrm{I} \equiv \int ds$ has an extreme or minimum value (zero) when extended over a light-ray. For this reason, these lines of zero length are known as minimal geodesics. However, the usual method of the Calculus of Variations for determining the differential equations of the geodesics is not immediately applicable. In this method we express the co-ordinates of a point in terms of two *independent* parameters τ and α :

$$x_r \equiv x_r(\tau, \alpha) \quad (r=1\ldots4).$$

The value of α being assigned, we have on varying τ a *particular* curve C_α, and when the integral $\mathrm{I}(\alpha)$ extended over this curve, $\alpha=0$ let us say, has an extreme value, $\delta\mathrm{I}$ $\left(\text{which is defined as } \equiv \left(\frac{\partial \mathrm{I}}{\partial \alpha}\right)_{\alpha=0} d\alpha\right)$ is zero,—*granting that* $\mathrm{I}(\alpha)$ *has a Taylor development near* $\alpha=0$ which requires the existence of the derivative $\left(\frac{\partial \mathrm{I}}{\partial \alpha}\right)_{\alpha=0}$. However, in the particular problem confronting us,

$$\mathrm{I}(\alpha) \equiv \int \sqrt{g_{mn} x_m' x_n'}\, d\tau \qquad (m, n \text{ umbral}),$$

where $x_m \equiv x_m(\tau, \alpha)$ and primes denote differentiations with respect to τ, and

$$\frac{\partial \mathrm{I}}{\partial \alpha} \equiv \int \left\{ \frac{1}{2} \frac{\partial}{\partial \alpha} (g_{mn} x_m' x_n') / \sqrt{g_{mn} x_m' x_n'} \right\} d\tau$$

is not defined at $\alpha=0$ on account of the zero factor $(\sqrt{g_{mn} x_m' x_n'})_{\alpha=0}$ occurring in the denominator *. This

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* This is the reason for Eddington's remark (Report, p. 55) that "the notion of a geodesic fails for motion with the speed of light." This statement seems unfortunate, since the curves are uniformly referred to by geometers as "minimal geodesics."

difficulty may be overcome * by considering, instead of the arc integral, the integral

$$\bar{I}(\alpha) \equiv \int \left(\frac{ds}{d\tau}\right)^2 d\tau \equiv \int_{C_\alpha} (g_{mn} x_m' x_n')\, d\tau.$$

No matter what the parameter τ is, this has an extreme value (zero) when extended over a light-ray, since the quadratic form $(ds)^2$ is supposed one-signed. (In the discussion of the *non*-minimal geodesics which give the path of a material particle it was convenient † to take for τ the arc length along the extremal; but this cannot be done here, since this length is no longer a variable but a constant—zero.) Writing for convenience $g_{mn} x_m' x_n' = F$, we find

$$\delta\bar{I} \equiv \left(\frac{\partial \bar{I}}{\partial \alpha}\right)_{\alpha=0} d\alpha \equiv \left\{ \int_{C_\alpha} \left(\frac{\partial F}{\partial x_r} \cdot \frac{\partial x_r}{\partial \alpha} + \frac{\partial F}{\partial x_r'} \frac{\partial^2}{\partial \alpha \partial \tau} x_r \right) d\tau \right\}_{\alpha=0} d\alpha,$$

the limits of the integral being independent of α ‡. On integrating the second term of the integrand by parts, after interchanging the order of differentiation with respect to α and τ, we find

$$\delta\bar{I} \equiv \frac{\partial F}{\partial x_r'} \delta x_r \Big|_1^2 + \int_C \left(\frac{\partial F}{\partial x_r} - \frac{d}{d\tau} \frac{\partial F}{\partial x_r'} \right) \delta x_r$$

(r umbral),

where the symbols 1, 2 refer to the ends of the curve and $\delta x_r \equiv \left(\frac{\partial x_r}{\partial \alpha}\right)_{\alpha=0} d\alpha$. If the ends are first kept fixed, we get the familiar Euler-Lagrangian equations

$$\frac{\partial F}{\partial x_r} - \frac{d}{d\tau} \frac{\partial F}{\partial x_r'} = 0\,;$$

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* *Cf.* Weyl, H., *Raum, Zeit, Materie*, Dritte Auflage (Berlin, 1919), p. 210.

Attention is directed to the fact that the integral $\bar{I}(\alpha)$ is not, properly speaking, a line integral attached to the curve $C(\alpha)$. Its value depends *not merely* on the curve $C(\alpha)$ alone, but on the particular parameter τ chosen to specify points on it.

† Eddington's Report, p. 48.

‡ This does not imply that the end-points of all the curves C_α coincide. Although τ takes the same values at these end-points, the functions $x_r \equiv x_r(\tau, a)$ do not necessarily do this, since there is a second variable α on which they depend.

and then allowing the ends to vary, we get the *additional end* condition

$$\frac{\partial F}{\partial x_r'}\,\delta x_r\Big|_1^2.$$

If a particular x_r does not appear in F, the corresponding Euler-Lagrangian equation gives at once $\dfrac{\partial F}{\partial x_r'}=$ const.; and so, if the *other* co-ordinates of the end-points are kept fixed, we find $\delta x_r\Big|_1^2=0$, provided the constant $\dfrac{\partial F}{\partial x_r'}$ is not zero. This may be conveniently written $\delta\int_1^2 dx_r=0$. This is the explanation of Eddington's statement * that a light-ray "is determined by stationary values of $\int dt$ instead of $\int ds$." In the special case of the solar gravitational field

$$F\,.\,(\delta\tau)^2\equiv(ds)^2\equiv(1-2m/r)(dt)^2-(1-2m/r)^{-1}(dr)^2$$
$$-r^2(d\theta)^2-r^2\sin^2\theta\,(d\phi)^2$$

does not involve t, and $\dfrac{\partial F}{\partial t'}\equiv 2(1-2m/r)t'\neq 0$ as t is not constant along the light-ray; so that $\delta\int_1^2 dt=0$, which is known as a Fermat or Huygens's Principle of Least Time. The space co-ordinates r, θ, ϕ of the end-points remain fixed: it may be observed that since ϕ does not occur in F, we have equally well $\delta\int_1^2 d\phi=0$ along the world line of a light pulse, the co-ordinates r, θ of the end-points being fixed, as also the time of departure and arrival of the pulse. We shall not make any use of this Fermat Least-Time Principle, but think it worth while to point out its exact significance.

§ 2. *Determination of the Elliptic Integral giving the Displacement.*

A first integral of the Euler-Lagrangian equations is immediately found. F being homogeneous of degree 2

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* Report, p. 55. The writer does not see how this "end-condition" can of itself replace the Euler-Lagrange differential equations. If, for example, we are investigating the shortest distance from a point to a curve in the ordinary Euclidean plane, the Euler-Lagrangian equations tell us that the curve must be linear (using Cartesian co-ordinates), whilst the end-condition says it must be at right angles to the original curve: quite a different kind of statement altogether.

in the x_r', we have (by Euler's Theorem on homogeneous functions, or directly)

$$x_r' \frac{\partial \mathrm{F}}{\partial x_r'} \equiv 2\mathrm{F} \qquad (r \text{ umbral}).$$

On multiplying, then, the equations $\frac{\partial \mathrm{F}}{\partial x_r} - \frac{d}{d\tau}\left(\frac{\partial \mathrm{F}}{\partial x_r'}\right) = 0$ by x_r', and using r as an umbral symbol, we find

$$\frac{\partial \mathrm{F}}{\partial x_r} x_r' - \frac{d}{d\tau}(2\mathrm{F}) + \frac{\partial \mathrm{F}}{\partial x_r'} x_r'' = 0, \quad \text{or} \quad \frac{d\mathrm{F}}{d\tau} = 0,$$

verifying the fact that F is constant along the extremals—the constant in the case of the minimal geodesics being zero. The differential equations are

$$\left(\frac{\partial}{\partial x_r} g_{mn}\right) x_m' x_n' = \frac{d}{d\tau} \cdot (2 g_{rn} x_n')$$

$$= 2 g_{rn} x_n'' + 2 \frac{\partial g_{rn}}{\partial x_m} x_m' x_n'$$

$$(m,\ n \text{ umbral}),$$

or

$$g_{rn} x_n'' + [mn,\, r]\, x_m' x_n' = 0,$$

since

$$\left(\frac{\partial g_{rn}}{\partial x_m} + \frac{\partial g_{rm}}{\partial x_n}\right) x_m' x_n' = 2 \frac{\partial g_{rn}}{\partial x_m} x_m' x_n'.$$

On multiplying by g^{rp} and using r as an umbral symbol, this gives

$$x_p'' + \{mn,\, p\}\, x_m' x_n' = 0.$$

Writing, for convenience,

$$\mathrm{F} \equiv g_4(t')^2 + g_1(r')^2 + g_2(\theta')^2 + g_3(\phi')^2,$$

we have, on account of the absence of t and ϕ from F, the integrals

$$\frac{\partial \mathrm{F}}{\partial t'} = \text{const.}\,; \quad \frac{\partial \mathrm{F}}{\partial \phi'} = \text{const.}$$

or

$$g_4 t' = \text{const.}\,; \quad g_3 \phi' = \text{const.},$$

which give, on substituting the values of g_4 and g_3,

$$(1 - 2m/r)t' = \mathrm{C}\,; \quad r^2 \sin^2\theta \,.\, \phi' = h,$$

where C and h are constants. The equation for θ is found, by writing $p = 2$ in

$$x_p'' + \{mn,\, p\}\, x_m' x_n' = 0,$$

to be

$$\frac{d}{d\tau}(r^2\theta') - r^2 \sin\theta \cos\theta\, (\phi')^2 = 0\ ^{*}\,;$$

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* *Cf.* Eddington's Report, Equation (30.12), p. 49.

on eliminating the parameter τ by means of $r^2 \sin^2\theta \,.\, \phi' = h$, we find without difficulty, since $\dfrac{d}{d\tau} \equiv \dfrac{h}{r^2 \sin^2\theta}\dfrac{d}{d\phi}$,

$$\frac{d^2\theta}{d\phi^2} - 2\cot\theta\left(\frac{d\theta}{d\phi}\right)^2 = \sin\theta\cos\theta,$$

which simplifies on writing $z = \cot\theta$ to

$$\frac{d^2z}{d\phi^2} + z = 0.$$

Hence, if initially $z=0$, $\dfrac{dz}{d\phi}=0$, $z \equiv 0$. Choosing accordingly our co-ordinates so that initially $\theta = \pi/2$, $\dfrac{d\theta}{d\phi}=0$, we have $\theta \equiv \pi/2$, and our integrals simplify to

$$r^2\phi' = h; \quad (1-2m/r)t' = \mathrm{C},$$

to which we add $\mathrm{F}=0$, or

$$(1-2m/r)(t')^2 - (1-2m/r)^{-1}(r')^2 - r^2(\phi')^2 = 0.$$

On writing $u = \dfrac{1}{r}$ and again eliminating τ, we find

$$\left(\frac{du}{d\phi}\right)^2 + u^2 = 2mu^3 + \frac{\mathrm{C}^2}{h^2}$$

or

$$\left(\frac{du}{d\phi}\right)^2 = 2mu^3 - u^2 + \frac{\mathrm{C}^2}{h^2}.$$

Here m is the gravitational mass of the sun, which has the dimensions of any one of the co-ordinates * (the velocity of light tends to unity as $r \rightarrow \infty$, so that a time-unit of 1 cm. $= \frac{1}{3} \,.\, 10^{-10}$ second). Taking, with Eddington, the kilometre as the unit of length, $m = 1{\cdot}47$; the smallest value that r can have for the light-pulse is equal to the radius of the sun, or 697,000. Hence we obtain a first approximation to the light-ray on neglecting the term in u^3 in comparison with that in u^2, and find immediately

$$u = \frac{\mathrm{C}}{h}\sin(\phi - \phi_0),$$

where ϕ_0 is a constant of integration. (This would be the equation of a straight line if the space were Euclidean,

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* If the gravitational constant of Newtonian mechanics is regarded as a *mere number*, mass has the dimensions $\mathrm{L}^3\mathrm{T}^{-2} = \mathrm{L}$ if L and T have the same dimensions.

the perpendicular distance from the origin being h/C). Hence $\frac{C}{h}$ is the largest value of u; so that it is a small quantity of the order $\frac{1}{7}.10^{-5}$. We shall denote this small quantity by α, and for the next approximation shall keep in any expression only the lowest powers of α occurring in it.

The discriminant of the literal cubic equation

$$a_0 x^3 + a_1 x^2 + a_2 x + a_3 = 0$$

is $$a_1^2 a_2^2 + 18 a_0 a_1 a_2 a_3 - 4 a_0 a_2^3 - 4 a_1^3 a_3 - 27 a_0^2 a_3^2.$$

For the cubic in question

$$2mu^3 - u^2 + \alpha^2 = 0;$$

this is $4\alpha^2(1-27m^2\alpha^2)$, which is positive since α is small.

Hence the three roots of the cubic are real; when $\alpha=0$ they are $0, 0, \frac{1}{2m}$, and writing as *first approximations* when α is small, $k_1\alpha$, $k_2\alpha$, $\frac{1}{2m}+k_3\alpha$, we find from the symmetric functions of the roots

$$k_1+k_2+k_3 = 0; \quad (k_1+k_2)\frac{\alpha}{2m} = 0; \quad k_1 k_2 \alpha^2 = -\alpha^2,$$

so that
$$k_3 = 0, \quad k_1 = -1, \quad k_2 = 1,$$

and we may write the three roots as

$$u_1 = -\alpha; \quad u_2 = +\alpha; \quad u_3 = \frac{1}{2m}\text{*}.$$

The next approximation is found in the same way or by direct substitution in the cubic to be

$$u_1 = -\alpha + m\alpha^2; \quad u_2 = \alpha + m\alpha^2; \quad u_3 = \frac{1}{2m} - 2m\alpha^2.$$

Now the cubic $\left(\frac{du}{d\phi}\right)^2 = 2mu^3 - u^2 + \alpha^2$ cannot be negative in our physical problem, whilst also u starts out very small and is always positive. As the ray of light is traced out, u starts at zero (let us say) and increases to u_2, at which value $\left(\frac{du}{d\phi}\right)$ is zero and u has a maximum value corresponding to the perihelion of the light-path. The variable u must then retrace its values (it cannot lie between u_2 and u_3,

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[*] It is just as convenient to substitute the trial solutions $\frac{1}{2m}+k\alpha$, etc., directly in the cubic, and thus determine the k.

since values between these roots make the cubic negative), the sign of the radical changing as u passes through the value u_2. Accordingly as u varies from u to u_2, the angle ϕ traces out the angle to the perihelion from a remote distance. The excess of twice this angle over π gives the amount of deflexion of the ray. Solving for $d\phi$, we have as the required deflexion

$$\mathrm{D} = 2\int_0^{u_2} \frac{du}{\sqrt{2mu^3 - u^2 + \alpha^2}} - \pi.$$

§ 3. *Evaluation of the Elliptic Integral for the Deflexion.*

It is convenient to make a simple linear change of variable under the sign of integration. We write $u = a + bz$ and determine the coefficients a and b of the transformation so that to the roots u_1 and u_2 of the cubic will correspond values 0 and 1 of z respectively. The values are $a = u_1$; $b = u_2 - u_1$, and then the third root u_3 goes over into $\frac{1}{k^2}$, where $k^2 = (u_2 - u_1)/(u_3 - u_1)$. The cubic $2mu^3 - u^2 + \alpha_2$ transforms into $2mb^3 z(1-z)\left(\frac{1}{k^2} - z\right)$, so that

$$\mathrm{D} = \frac{2k}{\sqrt{2mb}} \int_{-a/b}^{1} \frac{dz}{\sqrt{z(1-z)(1-k^2 z)}} - \pi.$$

This simplifies considerably on writing $z = \sin^2\theta$, when, in fact,

$$\mathrm{D} = \frac{4k}{\sqrt{2mb}} \int_{\sin^{-1}\sqrt{-\frac{a}{b}}}^{\pi/2} \frac{d\theta}{\sqrt{1 - k^2 \sin^2\theta}} - \pi.$$

Now $k^2 = \dfrac{u_2 - u_1}{u_3 - u_1} = \dfrac{2\alpha}{\frac{1}{2m} + \alpha}$ (to a first approximation) is a small quantity of the same order of magnitude as α. Hence we can expand $(1 - k^2\sin^2\theta)^{-\frac{1}{2}}$ in a rapidly convergent series, and a mere integration of the initial terms will give a very good approximation to D. The multiplier of the integral in D is $4k/\sqrt{2mb} = 4\sqrt{\dfrac{1}{2m(u_3 - u_1)}}$ from the expressions for k and b. From the values given for u_3 and u_1 this is $4(1 + 2m\alpha)^{-\frac{1}{2}} = 4(1 - m\alpha)$. The lower limit of the integral is $\sin^{-1}\sqrt{\dfrac{u_1}{u_1 - u_2}} = \sin^{-1}\sqrt{\frac{1}{2}(1 - m\alpha)}$, where

here it will be observed that it is necessary to use the second approximation for u_1, since it is to be divided by $u_1 - u_2 - \ldots$, a small quantity of the first order. This may be written $\sin^{-1} \frac{1}{\sqrt{2}}\left(1 - \frac{m\alpha}{2}\right)$, and expanding $\sin\left(\frac{\pi}{4} + \epsilon\right)$ by the Taylor theorem, we see that the lower limit is $\frac{\pi}{4} - \frac{m\alpha}{2}$. Using the well-known result that $\int \sin^2\theta \, d\theta = \frac{1}{2}(\theta - \sin\theta\cos\theta)$, we find

$$D + \pi = 4(1 - m\alpha)\Big[\theta + \tfrac{1}{4}k^2(\theta - \sin\theta\cos\theta) \ldots\Big]_{\frac{\pi}{4} - \frac{m\alpha}{2}}^{\pi/2},$$

where, to a first approximation, $k^2 = 4m\alpha$. In the term multiplied by k^2 it is sufficient to use for the lower limit the rough approximation $\frac{\pi}{4}$, and we have

$$\begin{aligned} D + \pi &= 4(1 - m\alpha)\left[\frac{\pi}{4} + \frac{m\alpha}{2} + m\alpha\left(\frac{\pi}{4} + \tfrac{1}{2}\right)\right] \\ &= (1 - m\alpha)[\pi + m\alpha(4 + \pi)] \\ &= \pi + 4m\alpha + \ldots. \end{aligned}$$

Hence the deflexion D is $4m\alpha$, where α is to a first approximation the largest value u_2 of u: that is, the reciprocal of α is the smallest value of the distance r from the attracting centre to the light-ray. The closeness of the approximation is easily seen by taking the second approximation $u_2 = \alpha + m\alpha^2$, giving, on solving this quadratic for α,

$$2m\alpha = -1 + (1 + 4mu_2)^{\frac{1}{2}} = 2mu_2 - 2m^2u_2^2,$$

whence

$$\alpha = u_2 - mu_2^2 = \frac{1}{R}\left(1 - \frac{m}{R}\right);$$

$R \equiv \frac{1}{u_2}$ being the sun's radius.

Hence writing $\alpha = \frac{1}{R}$ gives us an accuracy which allows an error of about 1 in $5 . 10^5$, since $m = 1{\cdot}47$ and $R = 697{,}000$. On substituting these values in $D = \frac{4m}{R}$ and converting radian measure into seconds of arc, we recover Einstein's prediction of a deflexion of about $1''{\cdot}73$ for a ray which just grazes the sun.

Johns Hopkins University, Baltimore,
July 11th, 1921.

LXIX. *The Effect of Variable Specific Heat on the Discharge of Gases through Orifices or Nozzles.* By WILLIAM J. WALKER, *Ph.D., University College, Dundee* *.

SUMMARY. The following paper raises the question whether or not it is desirable to account for abnormal orifice or nozzle discharges by the consideration of changes in the value of γ, the index in the equation $pv^{\gamma}=\text{constant}$, for adiabatic changes of state. This appears, generally, to have been the custom hitherto, but, since the actual adiabatic equation under linear variable specific heat conditions is $pv^{m}e^{\lambda T}=\text{constant}$, the analysis in this paper has been carried out on the latter basis for the purpose of determining, as nearly as possible, what effect such specific heat variation has on discharges. An exact solution does not appear to be derivable, but the method of analysis adopted here may be carried to any degree of accuracy required. The method of analysis is somewhat similar to that adopted in a previous paper dealing with another effect of variable specific heat. The result obtained in the present paper brings out prominently the fact that the error in computing discharges, by the usual constant specific heat theory, increases as the density of the medium in the reservoir is diminished. This fact appears to have been neglected in previous considerations of the subject. It is pointed out, also, that, by means of the discharge formulæ obtained, the method of orifice discharge may be used as a reliable and convenient one for the determination of specific heat variations with temperature.

IN the flow of gases through nozzles and orifices the analysis generally applied to any interpretation of test results is that based on the constancy of the specific heat of the gas concerned. The formulæ derived under such an assumption are, for the velocity of the gas,

$$u_c=\left[2g\frac{\gamma}{\gamma-1}p_1v_1\{1-x^{\frac{\gamma-1}{\gamma}}\}\right]^{\frac{1}{2}} \text{ feet per sec.,} \quad . \quad (1)$$

and for the quantity discharged,

$$Q_c=A\left[2g\frac{\gamma}{\gamma-1}\frac{p_1}{v_1}(x^{\frac{2}{\gamma}}-x^{\frac{\gamma+1}{\gamma}})\right]^{\frac{1}{2}} \text{ lb. per sec.,} \quad . \quad (2)$$

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* Communicated by the Author.

where p_1 is the pressure in the reservoir in lb. per sq. ft. abs.
v_1 is the specific volume of the gas in the reservoir in cubic feet per lb.,

$$x=\frac{p}{p_1}=\frac{\text{pressure at discharge}}{\text{pressure in reservoir}}.$$

The suffix c in u_c and Q_c refers to the constancy of specific heat as assumed in the derivation of these formulæ.

In applying the foregoing equations (1) and (2) to experimental results it is customary to account, by one means at least, for departures from theoretical discharges by a suitable variation of γ. Such a procedure can scarcely be called a satisfactory one, and it is proposed in what follows to deduce a rational formula (assuming, at first, *linear* variable specific heat conditions) which will require no such adjustment. This can then be extended to include quadratic variable specific heat conditions and so on for any variation of specific heat with temperature of the form $K=a+bT+cT^2+dT^3+\ldots$ which may be specified.

In the adiabatic expansion of a gas, the velocity at any cross-section of the stream is given by

$$u^2=2gK_p\int_T^{T_1}dT \text{ feet per sec.}, \quad . \quad . \quad . \quad (3)$$

assuming a reservoir of infinite capacity, K_p being the specific heat at constant pressure, in ft. lb. per lb. per degree centigrade, T being temperature in degrees centigrade absolute

Let
$$K_p=A+ST,$$
$$K_v=B+ST,$$

K_v being the specific heat at constant volume.

Also, let
$$m=\frac{A}{B},$$

and
$$\lambda=\frac{S}{B}.$$

$$\therefore \quad u^2=2g\left[A\{T_1-T\}+\frac{S}{2}\{T_1^2-T^2\}\right]$$

$$=2g\frac{m}{m-1}\{p_1v_1-pv\}\left\{1+\frac{\lambda}{2mR}(p_1v_1+p_2v_2)\right\}. \quad (4)$$

Now, during adiabatic changes of state

$$pv^m e^{\lambda T}=\text{constant}.$$

$$\therefore \quad \frac{v}{v_1}=\left(\frac{p_1}{p}\right)^{\frac{1}{m}}\left\{1+\frac{\lambda}{m\mathrm{R}}(p_1v_1-pv)\right\}$$

to a first appromimation

$$=\left(\frac{p_1}{p}\right)^{\frac{1}{m}}\times f. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

Equation (4) may therefore be written

$$u^2=2g\frac{m}{m-1}p_1^{\frac{1}{m}}v_1\{p_1^{\frac{m-1}{m}}-p^{\frac{m-1}{m}}\times f\}$$

$$\left\{1+\frac{\lambda p_1^{\frac{1}{m}}v_1}{2m\mathrm{R}}\left(p_1^{\frac{m-1}{m}}+p^{\frac{m-1}{m}}\right)\right\}$$

$$=2g\frac{m}{m-1}p_1^{\frac{1}{m}}v_1\left\{p_1^{\frac{m-1}{m}}-p^{\frac{m-1}{m}}-\frac{\lambda p^{\frac{m-1}{m}}p_1^{\frac{1}{m}}v_1}{m\mathrm{R}}\right.$$

$$\left.\left(p_1^{\frac{m-1}{m}}-p^{\frac{m-1}{m}}\right)\right\}\left\{1+\frac{\lambda\phi}{m\mathrm{R}}\right\},$$

where $\phi=p_1^{\frac{1}{m}}v_1\left(p_1^{\frac{m-1}{m}}+p^{\frac{m-1}{m}}\right)$.

$$\therefore \quad u^2=2g\frac{m}{m-1}p_1^{\frac{1}{m}}v_1\left(p_1^{\frac{m-1}{m}}-p^{\frac{m-1}{m}}\right)$$

$$\left\{1-\frac{\lambda}{\mathrm{R}}p^{\frac{m-1}{m}}p_1^{\frac{1}{m}}v_1\right\}\left(1+\frac{\lambda\phi}{m\mathrm{R}}\right)$$

$$=2g\frac{m}{m-1}p_1^{\frac{1}{m}}v_1\left(p_1^{\frac{m-1}{m}}-p^{\frac{m-1}{m}}\right)$$

$$\left\{1+\frac{\lambda}{\mathrm{R}}\left(\frac{\phi}{2m}-\frac{p^{\frac{m-1}{m}}p_1^{\frac{1}{m}}v_1}{m}\right)\right\} \text{ to a first approximation}$$

$$=2g\frac{m}{m-1}p_1^{\frac{1}{m}}v_1\left(p_1^{\frac{m-1}{m}}-p^{\frac{m-1}{m}}\right)$$

$$\left\{1+\frac{\lambda p_1^{\frac{1}{m}}v^1}{2m\mathrm{R}}\left(p_1^{\frac{m-1}{m}}-p^{\frac{m-1}{m}}\right)\right\}$$

$$=2g\frac{m}{m-1}p_1v_1\left\{1-x^{\frac{m-1}{m}}\right\}\left\{1+\frac{\lambda\mathrm{T}_1}{2m}\left(1-x^{\frac{m-1}{m}}\right)\right\}.$$

$$\therefore \quad u^2=u_c^2\left\{1+\frac{\lambda\mathrm{T}_1}{2m}\left(1-x^{\frac{m-1}{m}}\right)\right\} \text{ to a first approximation,}$$

$$i.e. \quad u=u_c\left\{1+\frac{\lambda\mathrm{T}_1}{4m}\left(1-x^{\frac{m-1}{m}}\right)\right\}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

But $Q^2 = \dfrac{A^2u^2}{v^2}$ and $v^2 = \dfrac{f^2v_1{}^2}{x^{\frac{2}{m}}}$ from (5).

$$\therefore\quad Q^2 = 2g\frac{m}{m-1}A^2\frac{p_1}{v_1}\left\{x^{\frac{2}{m}} - x^{\frac{m+1}{m}}\right\}$$

$$\left\{1 - \frac{3}{2}\frac{\lambda T_1}{m}\left(1 - x^{\frac{m-1}{m}}\right)\right\} \text{ to a first approximation.}$$

$$\therefore\quad Q = Q_c\left\{1 - \frac{3}{4}\frac{\lambda T_1}{m}\left(1 - x^{\frac{m-1}{m}}\right)\right\}. \quad \ldots\ldots \quad (7)$$

If, however, $K_p = A + ST + S'T^2$

and $K_v = B + ST + S'T^2$

with $\lambda' = \dfrac{S'}{B}$,

then the formulæ (6) and (7) become respectively

$$u = u_c\left\{1 + \left(\lambda T_1 + \frac{\lambda' T^2}{2}\right)\left(\frac{1 - x^{\frac{m-1}{m}}}{4m}\right)\right\}, \quad \ldots \quad (8)$$

and
$$Q = Q_c\left\{1 - 3\left(\lambda T_1 + \frac{\lambda' T^2}{2}\right)\left(\frac{1 - x^{\frac{m-1}{m}}}{4m}\right)\right\}. \quad \ldots \quad (9)$$

It will be observed from formulæ (6) to (9) that, when S (or what is the same thing, λ) is positive, the velocity u is greater under variable than under constant specific heat conditions, while Q, the quantity discharged, is less. The same applies, of course, to S′ and λ′. If λ and λ′ are negative, then the velocity u is less and the discharge Q is greater than under constant specific heat conditions.

The foregoing analysis suggests another method of specific heat determination, besides those already in use. By the provision of a suitably short convergent nozzle of invariable coefficient of contraction under all conditions, the application of equations (6) to (9) to the discharges obtained would enable the values of λ and λ′ to be derived. This method has, at least, decided advantages over most others, particularly in the simplicity both of the experimental work and calculations involved.

It is to be observed, of course, that the same qualification must be applied to these variable specific heat equations (6) to (9) as are applied to the usual constant specific heat formulæ. That is, they must be used as they stand, only for cases of flow in which the discharge pressure is above or equal to the critical pressure, *i. e.*, when the stream velocity at discharge is less than or equal to that of the velocity of sound through the gas under the discharge conditions which prevail. For discharge pressures below this value, the assumption (which is found to accord closely with experimental fact) is made that the maximum discharge value holds for all values of x.

Other points worth noting are:—

1. That the percentage error involved in the computation of discharges is three times the percentage error in velocity computations on a constant specific heat basis.
2. That the discharge error increases as x decreases while the velocity error also increases.
3. That the error in both velocity and discharge computations on a constant specific heat basis increases as the temperature of the gas in the reservoir is increased. In other words, for a given reservoir pressure p_1 the errors increase as the density of the gas in the reservoir is diminished.

The conclusions reached here with regard to the effect of variable specific heat on gas discharges are somewhat like those reached in a previous paper* by the writer on "The Effect of Variable Specific Heat on Thermodynamic Cycle Efficiencies." The equations deduced in that paper were of analogous form to those given here for orifice discharges. The applicability of the former to, and their value in, practical internal combustion work has since been fully demonstrated, and it is hoped that equations (6) to (9) may prove of equal value.

LXX. *The Motion of Electrons in Argon.* *By* J. S. Townsend, *M.A., F.R.S., Wykeham Professor of Physics, Oxford, and* V. A. Bailey, *M.A., Queen's College, Oxford* †.

1. IN the December number of the Philosophical Magazine we gave an account of the motion of electrons in nitrogen, hydrogen, and oxygen, and it was shown that the loss of energy of an electron in colliding with a molecule, and the mean free path of the electron, may be found from the experimental determinations of the velocity of the electron in the direction of the electric force and its velocity of agitation. We give in this paper the results of similar

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* Phil. Mag. Sept. 1917.

† Communicated by the Authors.

investigations with argon, which are of particular interest, as they show that the molecules of this gas are very different from those of the other gases.

Thus when an electron moving with a velocity of the order of 10^8 centimetres per second collides with a molecule of argon it loses about one ten-thousandth part of its energy, but when it collides with molecules of the other gases it loses more than one per cent. of its energy. Also the mean free path of an electron moving with these velocities in argon is about ten times as long as its mean free path in the other gases at the same pressure.

2. The experiments with argon were made with the apparatus described in the previous paper. Some preliminary investigations were made with impure argon which had been dried for several days in a vessel containing phosphorus pentoxide. The gas was supplied in a cylinder by the British Oxygen Company, and was said to contain 88 per cent. of argon, 10·5 per cent. of nitrogen, and 1·5 per cent. of oxygen. It was found that the lateral divergence of a stream of electrons in the impure argon was remarkably large, and for a given electric force X and gas pressure p the velocity in the direction of the electric force and the velocity of agitation of the electrons were greater than in nitrogen or hydrogen. The gas was then purified by Rayleigh's method. It was admitted to a pressure of about 50 centimetres into a flask containing a solution of caustic potash, and oxygen was admitted in excess of the amount required to combine with the nitrogen. Two platinum electrodes were sealed in the flask and a discharge was passed through the gas for several hours. An approximate estimate of the rate of combination of the oxygen and nitrogen was made by observing the change of pressure of the gas, and when the proportion of nitrogen was reduced to about one per cent. of the argon the gas was passed over hot copper in long quartz tubes to remove all the oxygen, and into a vessel containing phosphorus pentoxide, where it was dried for several days before measurements were made of its electrical properties.

As it was important that no air should leak into the gas all the apparatus, including the quartz tubes, had been exhausted by a mercury pump down to one-hundredth of a millimetre, and tested for leaks by a McLeod gauge. Also before using the copper it was heated for several hours in order to expel the occluded gases. This first purification did not have an appreciable effect on the velocity in the direction of the electric force, but the divergence of the stream of electrons became wider than in the more impure argon.

These results indicated that quantities of nitrogen of the order of one per cent. of the argon would have large effects on the velocities.

The gas was therefore purified a second time, the process being continued until the estimated quantity of nitrogen remaining in the gas was very much less than one-thousandth of the argon. The excess of oxygen was, in this case, removed by passing the gas over hot copper several times.

The second purification had the effect of *reducing* the velocity in the direction of the electric force and of making a further increase in the lateral divergence of the stream of ions.

3. The following examples of the measurements made with argon show how the velocities of the electrons are affected by reducing the proportion of nitrogen.

With the gas at a pressure of 20 millimetres and an electric force Z of 17 volts per centimetre the velocities W in the direction of the electric force were 22×10^5 cms. per second in impure argon, 22×10^5 cms. per second in argon containing about one per cent. of nitrogen, and $9{\cdot}3 \times 10^5$ cms. per second in argon containing less than a tenth of one per cent. of nitrogen. With the same force and pressure the quantities k representing the factor by which the mean energy of agitation $(mu^2/2)$ of an electron exceeds the mean energy of agitation of a molecule of a gas at 15° C. were 48·8, 73, and 155 in the three cases respectively.

For the ratio $Z/p = 17/20$ the velocities W in nitrogen and in hydrogen are $7{\cdot}6 \times 10^5$ and $11{\cdot}1 \times 10^5$ cms. per second and the values of k are 19 and 7·9 in the two gases respectively.

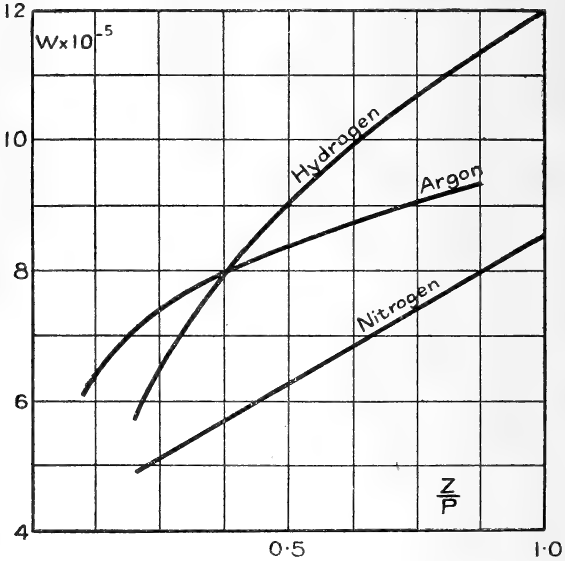
Owing to the very large divergence of the streams of electrons in argon it was impossible to make accurate measurements of the values of W and k corresponding to the lower pressures which were used in the experiments with nitrogen and hydrogen. In the experiments with the purest argon W and k were measured with pressures from 20 to 120 millimetres and with electric forces from 12 to 34 volts per centimetre, so that the experiments are over a range of comparatively small values of the ratio Z/p.

A new apparatus is being made which is suitable for cases where the streams of electrons are very divergent, and we hope to extend these experiments with a view to measuring the velocities of electrons in argon corresponding to a wider range of the ratio Z/p.

4. The velocities W, obtained with the argon which had been purified twice, are shown in terms of the ratio (Z/p) by a curve in fig. 1. The velocities W in nitrogen and hydrogen are also given by curves for comparison.

It will be seen that no great difference between the three gases is to be found from the measurements of the velocity W in the direction of the electric force alone.

Fig. 1.



The values of k for the pure argon, for nitrogen, and for hydrogen in terms of the ratio Z/p are given by the curves in fig. 2, which show a great difference between the three gases.

5. The velocity of agitation u of an electron, its mean free path l, and the proportion λ of the energy of an electron lost in a collision with a molecule of argon, are given in Table I. The numbers for W, l, and λ are obtained from the formulæ

$$u = 1{\cdot}15\times10^7\times\sqrt{k},$$

$$W = \frac{Z}{p}\times\frac{e}{m}\times\frac{lp}{u}\times{\cdot}815,$$

$$\lambda = 2{\cdot}46\times\frac{W^2}{u^2},$$

the numerical factor in the last formula being an approximate estimate as explained in the previous paper *.

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* Phil. Mag. Dec. 1921, p. 889.

Fig. 2.

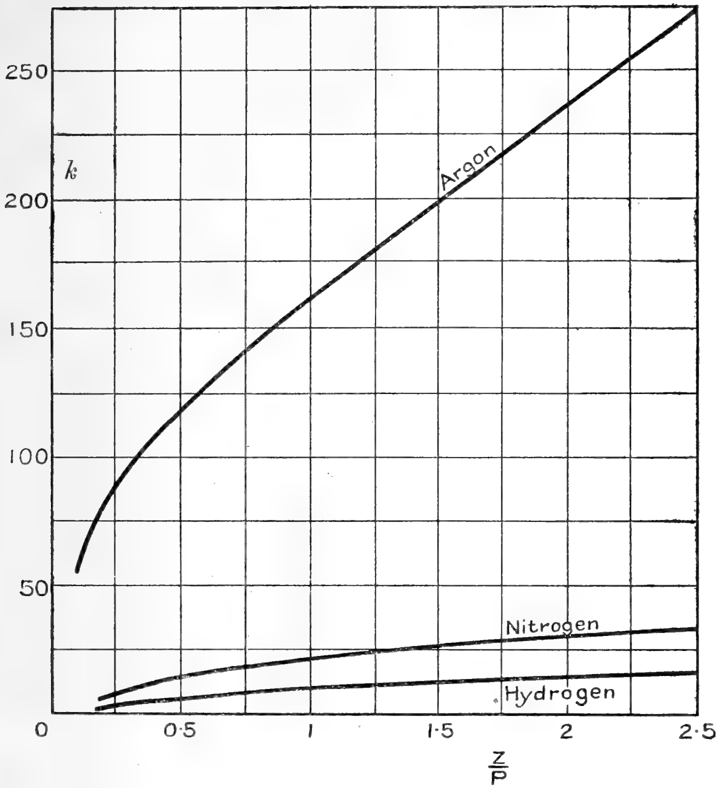

TABLE I.

Argon.

$\frac{Z}{p}$.	k.	$W \times 10^{-5}$.	$u \times 10^{-7}$.	$lp \times 100$.	$\lambda \times 10^4$.
2·5	275	—	19·1	—	—
2·0	237	—	17·7	—	—
1·5	200	—	16·3	—	—
1·0	162	—	14·6	—	—
·8	147	9·15	13·9	11·1	1·07
·6	129	8·65	13·1	13·3	1·08
·4	109	8·05	12·0	16·8	1·09
·3	96	7·65	11·3	20·2	1·12
·2	80	7·1	10·3	25·8	1·18
·1	55	6·05	8·5	36·3	1·24

6. Since the effect of a collision of an electron with a molecule depends on the velocity of the electron, it is of interest to compare the effects of collisions in argon, nitrogen, and hydrogen when the electrons are moving with the same velocity u. From the determinations that have been made the effects obtained in the three gases may be compared when the velocity of agitation is between $8{\cdot}5\times10^{7}$ and 14×10^{7} cms. per sec. The values of Z/p required to maintain the velocity of agitation u in each gas are given in Table II. with the corresponding values of the velocities W.

TABLE II.

$u\times10^{-7}$.	Argon.		Nitrogen.		Hydrogen.	
	Z/p.	$W\times10^{-5}$.	Z/p.	$W\times10^{-5}$.	Z/p.	$W\times10^{-5}$.
14	·82	9·15	74	215	57·3	255
12	·40	8·05	50·5	172	32·4	128
10	·19	7·05	32	124	19·2	69
8·5	·10	6·05	16	72	13·0	49

From the numbers given in Table II., the mean free paths l and the proportions of the energy of an electron lost in a collinson λ may be calculated by the preceding formulæ. These are given in Table III.

TABLE III.

$u\times10^{-7}$.	Argon.		Nitrogen.		Hydrogen.	
	$lp\times100$.	$\lambda\times10^{4}$.	$lp\times100$.	$\lambda\times10^{4}$.	$lp\times100$.	$\lambda\times10^{4}$.
14	10·8	1·05	2·85	580	4·35	815
12	16·8	1·09	2·86	505	3·32	280
10	26·9	1·19	2·71	380	2·52	117
8·5	36·3	1·24	2·68	177	2·25	82

These numbers show that the mean free path l of an electron is about ten times as long in argon as in hydrogen or nitrogen at the same pressure when the velocity is 10^{8} cms. per second. This result is remarkable, especially as the radii σ of the molecules as deduced from the viscosity of the gas are not much different, the values of $\sigma\times10^{8}$ being 1·80 cms. in argon, 1·88 cms. in nitrogen, and 1·34 cms. in hydrogen. Also there is a large increase in the free path l in argon as the velocity u of the electron is reduced. A similar effect was obtained in nitrogen, oxygen, and hydrogen with lower velocities. Thus in nitrogen at one millimetre pressure l increases from 0·266 mm. to 0·455 mm. when the velocity is reduced from $8·85 \times 10^7$ to $3·15 \times 10^7$ cm. per sec.

The values of λ for argon are very much less than for the other gases. They can only be considered as approximate values, owing to the large effect of impurities, one part of nitrogen to 10^5 of argon being sufficient to increase the value of λ for argon by 3 per cent. The values of λ for nitrogen and hydrogen diminish with the velocity u, and in nitrogen when $u = 4 \times 10^7$ cms. per sec. λ is $5·5 \times 10^{-4}$, which is still about five times as great as the value for argon with the velocity $u = 10^8$.

7. If the argon were absolutely pure, and if there were no loss of energy when an electron collides with a molecule of argon except the small loss corresponding to the momentum imparted to the molecule regarded as a perfectly elastic body, the value of λ would be about a quarter of the value found experimentally. The question therefore arises as to whether the amount of nitrogen remaining in the argon after the second purification would be sufficient to increase the value of λ from about $0·33 \times 10^{-4}$ to the observed value $1·2 \times 10^{-4}$.

The following calculations show what amount of nitrogen would be necessary to produce this effect. If the argon contained one molecule of nitrogen to 4000 molecules of argon, an electron would make one collision with a molecule of nitrogen for 400 collisions with molecules of argon, the velocity of the electron being about 10^8 cms. per second. If E be the energy of the electron, the average loss of energy in each collision with a molecule of nitrogen is $3·8 \times 10^{-2}$E, and in each collision with a molecule of argon the loss would be about 3×10^{-4}E, if the argon be supposed to be perfectly elastic. Thus the average loss of energy in a collision would be

$$0·3 \times 10^{-4}\mathrm{E} + 3·8 \times 10^{-2}\mathrm{E}/400,$$

and the value of λ would be $1·25 \times 10^{-4}$, which is near the observed value.

From the observations made on the contraction of the gas in the process of purification by sparking, we concluded that the proportion of nitrogen to argon remaining in the gas was much less than one part in 4000, but we cannot be certain that other impurities were present in a smaller proportion, so that notwithstanding the experimental results it may be possible that no part of the energy of the electron is transferred to the molecule in the form of internal energy.

We expect, however, to be able to obtain more definite evidence on this point, by extending the investigations over a larger range of the velocities of agitation u. The proportion of the energy of an electron lost in a collision with a molecule of nitrogen diminishes rapidly with the velocity of the electron, so that the value of λ for electrons moving in argon would be much less affected by a small proportion of nitrogen, if the determinations were made with velocities of agitation of about 4×10^7 cms. per second instead of the velocities given in Table III.

NOTE.

Since this paper was written we have noticed that Mayer* and Ramsauer† have determined the penetration of electrons in gases, and obtained estimates of the free paths of the electrons or cross sections of the molecules. They found that the free path in argon was about 15 times the free path in nitrogen or hydrogen. They also found that the free paths in argon were much increased when the velocity of the electrons was reduced from $6{\cdot}3\times10^7$ to $5{\cdot}2\times10^7$ cms. per sec. Ramsauer concluded that there was no noticeable change in the free paths of electrons in the other gases for similar changes in the velocity. The latter result is not in agreement with our determinations.

LXXI. *The Identical Relations in Einstein's Theory.* *By* G. B. JEFFERY, *M.A., D.Sc., Fellow of University College, London* ‡.

IN Einstein's general theory of relativity it is assumed that the gravitational field is completely defined by the coefficients $g_{\mu\nu}$ in the expression for the interval in the four-dimensional continuum,

$$\delta s^2 = g_{\mu\nu}\delta x_\mu \delta x_\nu . \qquad (1)$$

where, with the usual convention, the repetition of a suffix in the same term implies summation for values 1, 2, 3, 4 of that suffix.

It is further assumed that these coefficients satisfy the

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* H. F. Mayer, *Ann. d. Phys.* vol. lxiv. p. 451 (1921).
† C. Ramsauer, *Ann. d. Phys.* vol. lxiv. p. 513 (1921).
‡ Communicated by the Author.

tensor equation

$$G_{\mu\nu}-\tfrac{1}{2}g_{\mu\nu}G=-8\pi\kappa T_{\mu\nu}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $T_{\mu\nu}$ is a tensor expressing the density and motion of matter, κ is a constant, and

$$G_{\nu\mu}\equiv-\frac{\partial}{\partial x_\alpha}\{\mu\nu,\alpha\}+\{\mu\alpha,\beta\}\{\nu\beta,\alpha\}$$
$$+\frac{\partial^2}{\partial x_\mu\partial x_\nu}\log\sqrt{-g}-\{\mu\nu,\alpha\}\frac{\partial}{\partial x_\alpha}\log\sqrt{-g}, \quad . \quad (3)$$

in which g is the determinant of the $g_{\mu\nu}$, $g^{\mu\nu}$ is the co-factor of $g_{\mu\nu}$ divided by g, the Christoffel symbols are defined by

$$\{\mu\nu,\alpha\}=\tfrac{1}{2}g^{\alpha\beta}\left(\frac{\partial g_{\mu\beta}}{\partial x_\nu}+\frac{\partial g_{\nu\beta}}{\partial x_\mu}-\frac{\partial g_{\mu\nu}}{\partial x_\beta}\right), \quad . \quad . \quad (4)$$

and G is the scalar $g^{\mu\nu}G_{\mu\nu}$.

Further, it is found that the principles of the conservation of mass, energy, and momentum in their generalized form are expressed by the contracted covariant derivative equation

$$T^\nu_{\mu\nu}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

From (2) and (5) the following relations are deduced:

$$G^\nu_{\mu\nu}=\tfrac{1}{2}\frac{\partial G}{\partial x_\mu}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

in which the contracted covariant derivatives are defined by

$$G^\nu_{\mu\nu}=\frac{\partial G^\nu_\mu}{\partial x_\nu}-\{\mu\nu,\alpha\}G^\nu_\alpha+\{\alpha\nu,\nu\}G^\alpha_\mu, \quad . \quad . \quad (7)$$

where $G^\nu_\mu=g^{\nu\rho}G_{\mu\rho}$.

The four relations corresponding to $\mu=1, 2, 3, 4$ in (6), if they are true at all, must be identities derivable from (3). Written out in full they are extremely complicated, and Prof. Eddington's remark in his 'Space, Time, and Gravitation'—that he doubts "whether anyone has performed the laborious task of verifying these identities by straightforward algebra"—must have come as a challenge to many students of the subject. However, he himself has given an algebraic proof, which is not at all laborious, in the French edition of his work*. In the meantime we had obtained a proof which is perhaps a little shorter than Prof. Eddington's and may be easier to those English readers whose knowledge of the subject is based mainly upon his "Report." In view of

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* *Espace, Temps et Gravitation, Complément Mathématique*, p. 89.

the fundamental importance of these identities in the theory of Relativity, we venture to put forward this proof.

It is known that a transformation of coordinates may be found in an infinite number of ways so that at *one definite point* of the continuum the $g_{\mu\nu}$ and their first differential coefficients have prescribed values. Select a definite point of the continuum which we will call the origin, and if necessary make a transformation of coordinates, so that the first differential coefficients of the $g_{\mu\nu}$ all vanish at the origin. The differential coefficients of the second and higher orders will then in general not vanish at the origin. We will first show that in the new coordinates the relations (6) are identically satisfied at the origin.

In the case when the first differential coefficients of the $g_{\mu\nu}$ vanish, the Christoffel symbols also vanish at the origin, and we have from (7)

$$\begin{aligned} G^{\nu}_{\mu\nu} &= \frac{\partial}{\partial x_\nu} G^{\nu}_{\mu} = \frac{\partial}{\partial x_\nu} (g^{\nu\lambda} G_{\mu\lambda}) \\ &= g^{\nu\lambda} \frac{\partial G_{\mu\lambda}}{d x_\nu}. \end{aligned}$$

Substituting from (3) and omitting terms which obviously vanish on differentiation, we have

$$\begin{aligned} G^{\nu}_{\mu\nu} = -\tfrac{1}{2} g^{\lambda\nu} g^{\alpha\beta} \frac{\partial^2}{\partial x_\nu \partial x_\alpha} \left(\frac{\partial g_{\lambda\beta}}{\partial x_\mu} + \frac{\partial g_{\mu\beta}}{\partial x_\lambda} - \frac{\partial g_{\lambda\mu}}{\partial x_\beta} \right) \\ + g^{\lambda\nu} \frac{\partial^3}{\partial x_\lambda \partial x_\mu \partial x_\nu} \log \sqrt{-g}. \end{aligned}$$

The second and third terms in the bracket cancel on summation, and we have

$$G^{\nu}_{\mu\nu} = -\tfrac{1}{2} g^{\lambda\nu} g^{\alpha\beta} \frac{\partial^3 g_{\lambda\beta}}{\partial x_\mu \partial x_\nu \partial x_\alpha} + g^{\lambda\nu} \frac{\partial^3}{\partial x_\lambda \partial x_\mu \partial x_\nu} \log \sqrt{-g}. \quad (8)$$

Again,

$$\begin{aligned} \frac{\partial G}{\partial x_\mu} &= \frac{\partial}{\partial x_\mu} (g^{\lambda\nu} G_{\lambda\nu}) \\ &\left.\begin{aligned} = -\tfrac{1}{2} g^{\lambda\nu} g^{\alpha\beta} \frac{\partial^2}{\partial x_\mu \partial x_\alpha} \left(\frac{\partial g_{\lambda\beta}}{\partial x_\nu} + \frac{\partial g_{\nu\beta}}{\partial x_\lambda} - \frac{\partial g_{\lambda\nu}}{\partial x_\beta} \right) \\ + g^{\lambda\nu} \frac{\partial^3}{\partial x_\lambda \partial x_\mu \partial x_\nu} \log \sqrt{-g}. \end{aligned}\right\} \quad . \quad (9) \end{aligned}$$

The first and second terms are identical on summation ;

the third is

$$\tfrac{1}{2}g^{\lambda\nu}g^{\alpha\beta}\frac{\partial^3 g_{\lambda\nu}}{\partial x_\mu \partial x_\alpha \partial x_\beta}=\tfrac{1}{2}g^{\lambda\nu}g^{\alpha\beta}\frac{\partial^3 g_{\alpha\beta}}{\partial x_\lambda \partial x_\mu \partial x_\nu}$$
$$=\tfrac{1}{2}g^{\lambda\nu}\frac{\partial^2}{\partial x_\lambda \partial x_\mu}\left(g^{\alpha\beta}\frac{\partial}{\partial x_\nu}g_{\alpha\beta}\right)$$
$$=g^{\lambda\nu}\frac{\partial^3}{\partial x_\lambda \partial x_\mu \partial x_\nu}\log\sqrt{-g},$$

so that (9) gives

$$\frac{\partial G}{\partial x_\mu}=-g^{\lambda\nu}g^{\alpha\beta}\frac{\partial^3 g_{\lambda\beta}}{\partial x_\mu \partial x_\nu \partial x_\alpha}+2g^{\lambda\nu}\frac{\partial^3}{\partial x_\lambda \partial x_\mu \partial x_\nu}\log\sqrt{-g}. \quad (10)$$

Comparing (8) and (10), we see that the relations (6) in the new coordinates are identically satisfied at the origin. Being tensor relations, their validity is unaffected by a transformation of coordinates, and they are therefore identically satisfied in the original coordinates at the origin. But the origin is an arbitrary point of the continuum. Hence the relations in question are identically satisfied throughout the continuum.

These being proved, we may write (2)

$$-8\pi\kappa T_{\mu\alpha}=G_{\mu\alpha}-\tfrac{1}{2}g_{\mu\alpha}G,$$

and multiplying by $g^{\alpha\nu}$

$$-8\pi\kappa T^{\nu}_{\mu}=G^{\nu}_{\mu}-\tfrac{1}{2}g^{\nu}_{\mu}G.$$

Taking the contracted covariant derivative in accordance with (7), we have

$$-8\pi\kappa T^{\nu}_{\mu\nu}=G^{\nu}_{\mu\nu}-\tfrac{1}{2}g^{\nu}_{\mu}\frac{\partial G}{\partial x_\nu}$$
$$+\tfrac{1}{2}\{\mu\nu,\alpha\}g^{\nu}_{\alpha}G-\tfrac{1}{2}\{\alpha\nu,\nu\}g^{\alpha}_{\mu}G$$
$$=G^{\nu}_{\mu\nu}-\tfrac{1}{2}\frac{\partial G}{\partial x_\mu},$$

since $g^{\nu}_{\alpha}=0$, unless $\alpha=\nu$.

Hence, by the identical relations, we have $T^{\nu}_{\mu\nu}=0$, and the laws of energy and momentum are deduced as algebraic identities from Einstein's law of gravitation.

LXXII. *On the Mutual Induction between two Circular Currents.* *By* Dr. D. N. Mallik, *F.R.S.E.**.

1. THE mutual induction (M) between two circular currents i, i' in any relative position to each other is

$$4\pi^2 ii' c_1(1-\mu^2)(1-\mu'^2)\Sigma\left(\frac{c_1}{c_2}\right)^2 \frac{P_n \cos\theta}{n(n+1)} \frac{dP_n(\mu)}{d\mu} \frac{dP_n(\mu')}{d\mu'},$$

where c_1, c_2 are radii of the concentric spheres of which the circles are the cross-sections, $c_1 < c_2$ and $\theta =$ the inclination between the normals to the two circles.

2. If the circles are coplanar, then $\mu=0$, $\mu'=0$, $\theta=0$. Also

$$\frac{dP_{2m+1}(\mu)}{d\mu}_{(\mu=0)} = (-1)^m \cdot \frac{3.5.7.(2m+1)}{2.4.6\ldots 2m}.$$

If M_0 is the value of M in this case ($i=1=i'$), then

$$M_0 = 4\pi^2 c_2\left[\left(\frac{c_1}{c_2}\right)^2 \cdot \frac{1^2}{1.2} + \frac{1}{3.4}\left(\frac{c_1}{c_2}\right)^4 \cdot \frac{3^2}{2^2} + \ldots\right]$$

$$= 4\pi^2 c_2\left[2 \cdot \frac{c_1^2}{c_2^2}\frac{1^2}{2^2} + \frac{4}{3}\cdot\left(\frac{c_1}{c_2}\right)^4 \frac{1^2.3^2}{2^2.4^2} + \frac{6}{5}\cdot\left(\frac{c_1}{c_2}\right)^6 \cdot \left(\frac{1.3.5}{2.4.6}\right)^2 + \right].$$

But if V = gravitational potential of a wire of radius c_2 at a distance c_1 from the centre in the plane of the wire (density = 1),

$$V = 2\pi\left[1 + \frac{1^2}{2^2}\left(\frac{c_1}{c_2}\right)^2 + \frac{1^2.3^2}{2^2.4^2}\left(\frac{c_1}{c_2}\right)^4 + \ldots\right];$$

$$\therefore \quad 2\pi c_2 \frac{1}{c_1} \cdot \frac{\partial V}{\partial c_1} = \frac{\partial}{\partial c_1}\left(\frac{M_0}{c_1}\right). \quad \ldots \quad (1)$$

Now
$$V = \int \frac{c_2\, d\theta}{\sqrt{c_2^2 + c_1^2 - 2c_1c_2\cos\theta}}$$

$$= \frac{4c_2}{c_1+c_2}\int_0^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1-k^2\sin\phi}}$$

$$= 2(k'+1)\log\frac{4}{k'}\left(1 + \frac{1^2}{2^2}k_1^2 + \frac{1^2.3^2}{2^2.4^2}k'^4 + \ldots\right)$$

$$- \frac{1}{2^2}k'^2 \cdot \frac{2}{1.2} - \ldots,$$

where
$$k^2 = \frac{4c_1c_2}{(c_1+c_2)^2}$$

and
$$k' = \frac{c_2 - c_1}{c_1 + c_2} \text{ (assumed to be small).}$$

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* Communicated by the Author.

From (1) we get

$$2\pi\frac{k'+1}{1-k'}\frac{\partial \mathrm{V}}{\partial k'}=\frac{\partial\left(\frac{\mathrm{M}_0}{c_1}\right)}{\partial k'};$$

∴ we have

$$\mathrm{A}+\frac{\mathrm{M}_0}{c_1}=2\pi\left[\frac{k'+1}{1-k'}\mathrm{V}-\int 2\mathrm{V}\frac{\partial k'}{(1-k')^2}\right],$$

where A is the constant of integration.

Rejecting k'^2 and higher terms in the expression for V,

$$\mathrm{A}+\frac{\mathrm{M}_0}{c_1}=2\pi\frac{c_2}{c_1}\frac{4c_2}{c_1+c_2}\log\frac{4}{k'}-8\pi\int\left(\log\frac{4}{k'}\right)\frac{k'+1}{(1-k')^2}dk'$$

$$=\frac{8\pi c_2{}^2}{c_1(c_1+c_2)}\log\frac{4}{k'}+8\pi\int\log\frac{4}{k'}\,.\,(1+3k')dk'$$

$$=8\pi\frac{c_2{}^2}{c_1(c_1+c_2)}\log\frac{4}{k'}+8\pi\left[k'\log\frac{4}{k'}+k'\right.$$

$$\left.+\frac{3}{2}k'^2\log\frac{4}{k'}+\frac{3}{4}k'^2\right].$$

To determine the constant, we observe that the quantity independent of c_1 on the right-hand side is 8π. Hence, in view of the actual value of M_0, we get $\mathrm{A}=8\pi$.

Accordingly

$$\frac{\mathrm{M}}{c_1}=8\pi\left[\frac{c_2{}^2}{c_1+c_2}\log\frac{4}{k'}-1\right]+8\pi\left[k'\log\frac{4}{k'}+k'+\ldots\right].$$

It will be seen that if we put $c_2-c_1=x$, and reject powers about x^2, the first two terms reduce to $4\pi\left[c_2\log\frac{4}{k_1}-2\right]$, which agrees with Maxwell's result.

3. In the case of two parallel wires at a small distance apart, $\mu=0$, and we have

$$\mathrm{M}=4\pi^2c_1\Sigma\left(\frac{c_1}{c_2}\right)^2\frac{1}{n(n+1)}\left(\frac{d\mathrm{P}_n}{d\mu}\right)_0\left[\left(\frac{d\mathrm{P}_n}{d\mu}\right)_0\right.$$

$$+\frac{\partial}{\partial\mu'}\left[(1-\mu'^2)\frac{d\mathrm{P}_n}{d\mu'}\right]d\mu'+\frac{1}{2\,!}\frac{\delta^2}{\partial\mu'^2}\left[(1-\mu'^2)\frac{d\mathrm{P}_n}{d\mu'}\right]d\mu'^2+\ldots.$$

$$=\mathrm{M}_0-4\pi^2c_1\Sigma\left(\frac{c_1}{c_2}\right)^n.\left(\frac{d\mathrm{P}_n}{d\mu_0}\right)\left[\frac{1}{2\,!}\left(\frac{d\mathrm{P}_n}{d\mu'}\right)_0d\mu'^2\right.$$

$$\left.+\frac{1}{4\,!}\frac{d^3\mathrm{P}_n}{d\mu_0{}'^3}d\mu'^4+\ldots\right],$$

since

$$\left(\frac{d\mathrm{P}_n}{d\mu}\mathrm{P}_n\right)_0=0,$$

$$\left(\frac{d\mathrm{P}_n}{d\mu}\frac{d^2\mathrm{P}_n}{d\mu^2}\right)_0=0,\ \&\mathrm{c}.$$

Moreover, $$d\mu' = \frac{r}{c_1},$$

where r is the shortest distance between the wires.

The expression for μ can accordingly be expressed in the following symbolical form:—

We have

$$\left[\int_1^\rho e^{\rho \frac{d}{d\mu}} d\rho\right] P_n(\mu) = \left(\rho + \frac{\rho^2}{2\,!}\frac{d}{d\mu} + \ldots\right) P_n(\mu)$$

But $$\int_1^\rho e^{\rho \frac{d}{d\mu}} P_n(\mu)\,d\rho = \int_1^\rho P_n(\mu+\rho)\,d\rho\,;$$

i. e., $$\int_1^\rho P_n(\rho)\,d\rho = \left(\rho + \frac{\rho^2}{2\,!}\frac{d}{d\mu_0} + \ldots\right) P_n(0)$$

or $$\frac{1}{n(n+1)}\cdot \rho^2 \frac{dP_n(\rho)}{d\rho} = \left[P_n(0) + \frac{\rho^2}{2\,!}\frac{dP_n}{d\mu_0} + \ldots\right].$$

Hence

$$M = M_0 - 4\pi^2 c_1 \Sigma \left(\frac{c_1}{c_2}\right)^n \frac{1}{n(n+1)} \frac{dP_n}{d\mu_0} \cdot \frac{r^2}{c_1^2} \cdot \frac{dP_n\left(\frac{r}{c_1}\right)}{d\left(\frac{r}{c_1}\right)},$$

since $$\left(P_n \frac{dP_n}{d\mu}\right)_0 = 0, \text{ \&c.}$$

LXXIII. *Molecular Thermodynamics.* I. *By* BERNARD A. M. CAVANAGH, *B.A.*, *Balliol College, Oxford* [*].

I. THE GENERAL CONDENSED PHASE.

THE treatment of the thermodynamics of solutions given by Planck [†] for the simple limiting case of extreme dilution appears to be capable of extension to the general case. Planck himself, indeed, suggested [‡] the expansion of the specific Total-Energy and Volume of the solution, in integral powers of the various concentrations. But for general applicability this assumption of integral powers would appear to be quite unnecessarily arbitrary and narrow.

We have, in general, for the Total-Energy and Volume per unit quantity of solution, functions F_1 and F_2 (say) of the various concentrations, which will involve parameters dependent on Temperature and Pressure.

Now it would seem that the *minimum* assumption required

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[*] Communicated by Dr. J. W. Nicholson, F.R.S.

[†] 'Thermodynamics' (Trans. Ogg) 1917, Chap. v.

[‡] *Ibid.* p. 225.

to make possible an extension of Planck's method to the general case, is that F_1 and F_2 shall permit of expansion in the forms

$$\left.\begin{aligned} F_1 &= \Sigma u_x f_x\,(c_1 c_2 c_3 \ldots .) \\ F_2 &= \Sigma v_x f_x\,(c_1 c_2 c_3 \ \ldots .) \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1)$$

where f_1, f_2, . . . are functions *independent* of temperature and pressure, while u_1, $u_2 \ldots$, v_1, $v_2 \ldots$ are parameters dependent *only* on temperature and pressure.

Some of these parameters may of course be zero, since we use the same series of functions, f_1 $f_2 \ldots$, for both F_1 and F_2.

This *minimum* assumption is clearly a very wide one which will probably always be, at least very approximately, applicable.

Now as there can be little doubt that the linear form treated by Planck is the limiting form at the most extreme dilution, we may conveniently separate the simple linear terms from the rest which we shall call the "General terms":

$$F_1 = \Sigma u_1 c_1 + \Sigma u_x' f_x(c_1 c_2 \ldots .)$$
$$F_2 = \Sigma v_1 c_1 + \Sigma v_x' f_x(c_1 c_2 \ldots .).$$

The general terms must be of *degree higher than the first* in $c_1 c_2 \ldots .$, in order that the linear may be the limiting form.

For general treatment we may best express the concentrations as molecular ratios referred to the total number, n_t or Σn, of molecules, as denominator

$$c_1 = \frac{n_1}{n_t} = \frac{n_1}{\Sigma n} \text{ \&c.}$$

For special applications, as we shall see later, other "concentrations" may be preferable.

Taking the mean molecular weight in grams as the unit quantity of solution, and writing U and V for the Total-Energy and Volume of the whole solution,

$$\frac{U}{n_t} = \Sigma u_1 c_1 + \Sigma u_x' f_x(c_1 c_2 \ldots .),$$

$$\frac{V}{n_t} = \Sigma v_1 c_1 + \Sigma v_x' f_x(c_1 c_2 \ldots .),$$

that is

$$\left.\begin{aligned} U &= \Sigma n_1 u_1 + n_t \Sigma u_x' f_x(c_1 c_2 \ldots .) \\ V &= \Sigma n_1 v_1 + n_t \Sigma v_x' f_x(c_1 c_2 \ldots .) \end{aligned}\right\} \quad . \quad . \quad . \quad (2)$$

Now for a change of total Entropy while all the *n's* remain unchanged,

$$dS = \frac{dU + pdV}{T} = \Sigma n_1 \frac{du_1 + pdv_1}{T} + n_t \Sigma \frac{du_x' + pdv_x'}{T} f_x(c_1 c_2 \ldots)$$

$$= \Sigma n_1 ds_1 + n_t \Sigma (ds_x') f_x(c_1 c_2 \ldots .) \quad \ldots \ldots \quad (3)$$

Integrating,

$$S = \Sigma n_1 (s_1 + k_1) + n_t \Sigma (s_x' + k_x') f_x(c_1 c_2 \ldots .) \quad \ldots \ldots \quad (4)$$

The integration constants are determined by conceiving the system, by an ideal process of raising the temperature and diminishing the pressure, to pass into the perfect gaseous state, the number of the various molecules remaining unchanged.

It is not necessary that this should be practicable. The ideal process of "rushing" the system over the intervening unstable states, to exist, at least momentarily in the perfect gaseous state, all without appreciable change in the numbers of the various molecular species, is conceivable. It is not *intrinsically* impossible, or incompatible with our more limited experience, and that is all that is required.

For then, however momentarily, the entropy of the system will be expressible *both* by the integrated expression (4) and by the known expression for the entropy of a perfect gaseous mixture :

$$S = \Sigma n_1 [s_1 + l_1 - R \log c_1],$$

which gives us

$$k_1 = l_1 - R \log c_1,$$

$$k_x' = -s_x',$$

the latter s_x' corresponding to the ideal limiting state so that k_1' (etc.) like l_1 (etc.) and unlike k_1 (etc.), are independent of concentrations.

Returning now to our solution under ordinary conditions,

$$S = \Sigma n_1 (s_1 + l_1 - R \log c_1) + n_t \Sigma (s_x' + k_x')\, f_x(c_1 c_2 \ldots .),$$

and so

$$\psi = \left(S - \frac{U + pV}{T}\right) = n_1 (\psi_1 + l_1 - R \log c_1)$$

$$+ n_t \Sigma (\psi_x' + k_x') f_x(c_1 c_1 \ldots),$$

where ψ is the thermodynamic potential (of the dimensions of Entropy) used by Planck, which will be called simply "potential" throughout this paper.

We may write, more briefly,

$$\psi=\Sigma n_1(\phi_1-\mathrm{R}\log c_1)+n_t\Sigma\phi_x' f_x(c_1c_2\ldots.), \quad . \quad (5)$$

where every ϕ' as well as every ϕ is of the form

$$\phi_s=(\text{const.})-\frac{u_s+pv_s}{\mathrm{T}}+\int\frac{du_s+pdv_s}{\mathrm{T}}, \quad . \quad . \quad (6)$$

so that

$$\frac{\partial}{\partial p}\phi_s=-\frac{v_s}{\mathrm{T}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\frac{\partial}{\partial \mathrm{T}}\phi_s=\frac{u_s+pv_s}{\mathrm{T}^2}=\frac{q_s}{\mathrm{T}^2}, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$\mathrm{Q}=\mathrm{U}+p\mathrm{V}=\Sigma n_1(u_1+pv_1)+n_t\Sigma(u_x'+pv_x')f_x(c_1c_2\ldots)$$
$$=\Sigma n_1q_1+n_t\Sigma q_x' f_x(c_1c_2\ldots.). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The formal convenience of this use * of Q will appear clearly below.

Now from (5)

$$\frac{\partial\psi}{\partial n_s}=\phi_s-\mathrm{R}\log c_s+\Sigma\phi_x'\left[f_x+\frac{\partial f_x}{\partial c_s}-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right],$$

or writing, for convenience,

$$\left(f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right)=\mathrm{F}_x \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

we obtain

$$\frac{\partial\psi}{\partial n_s}=\phi_s-\mathrm{R}\log c_s+\Sigma\phi_x'\left[\mathrm{F}_x+\frac{\partial f_x}{\partial c_s}\right], \quad . \quad . \quad (11)$$

while from (9)

$$\frac{\partial \mathrm{Q}}{\partial n_s}=q_s \qquad +\Sigma q_x'\left[\mathrm{F}_x+\frac{\partial f_x}{\partial c_s}\right] \quad . \quad . \quad (12)$$

and from (3)

$$\frac{\partial \mathrm{V}}{\partial n_s}=v_s \qquad +\Sigma v_x'\left[\mathrm{F}_x+\frac{\partial f_x}{\partial c_s}\right] \quad . \quad . \quad (13)$$

We may now consider the general system of any number of components in any number of phases from the "molecular" point of view.

Any infinitesimal change in the molecular constitution of the system can be represented by $\Sigma\delta n_{1_a}$, where δn_{1_a} represents an *increment* of the number of molecules of the species (1) in

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* Planck writes Q for what will be δQ in this paper.

the phase (a). Clearly this covers chemical reactions as well as transferences between phases etc.

The *total Mass increase* of the system will be

$$\delta M = \Sigma m_{1_a} \delta n_{1_a} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The *total increase of Potential* will be

$$\delta\psi = \Sigma\left(\frac{\partial\psi}{\partial n_{1_a}}\right)\delta n_{1_a}. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The *total Heat Absorption* of the isothermal isopiestic change:

$$\delta Q = \Sigma\left(\frac{\partial Q}{\partial n_{1_a}}\right)\delta n_{1_a} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and the *total Dilatation* of the system :

$$\delta V = \Sigma\left(\frac{\partial V}{\partial n_{1_a}}\right)\delta n_{1_a}. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

It will be seen, of course, that equations (7–17) lead clearly and directly to the general thermodynamic relations

$$\frac{\partial}{\partial T}(\delta\psi) = \frac{1}{T^2}(\delta Q), \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$\frac{\partial}{\partial p}(\delta\psi) = -\frac{1}{T}(\delta V). \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Finally we have the conditions :—

For conservation of the mass of the system,

$$\delta M = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

For equilibrium (with regard to a particular virtual change)

$$\delta\psi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

II. MOLECULAR THERMODYNAMICS, VALUE AND GENERAL APPLICATION.

Strictly general thermodynamics is independent of atomic, molecular, or other hypotheses.

The term "Molecular Thermodynamics" is suggested and used here to signify a slightly less general treatment of thermodynamics which rests upon the molecular theory of matter. In the case of a low pressure gaseous phase the advantage of such treatment was early (though not perhaps explicitly) recognized.

Planck * first showed how it could be extended to condensed phases in the simple limiting case where one single

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* *Loc. cit.* chap. v.

molecular species vastly preponderates in each phase [*], the case in fact of very dilute solutions in non-associated, unmixed solvents [†].

In section I. above, the "molecular" treatment is extended to the perfectly general system of phases of any composition or state of aggregation, subject only to the very broad assumption (1).

That the "molecular" treatment when possible is essentially a step towards simplicity can scarcely be doubted, but apart from this, it appears to the author that the great importance and value of what is here called "Molecular thermodynamics" lies in the fact, apparently not recognized so far, that by expressing the Total-Energy in terms of the concentrations of the various molecular species (instead of, as in general thermodynamics, in terms of the concentrations of the *components*) *we relegate all the chemical energy entirely to the linear terms.*

The "general terms" must be considered to represent only potential [‡] energy of physical intermolecular forces. This suggests at once the possible use of Dynamical theory, which is, at least theoretically, applicable to the calculation of such energy. In section V. a striking and important example of the realization of this possibility will be given.

As regards the general application of molecular thermodynamics, the determination of $\delta\psi$, δQ, δV, for various isothermal isopiestic changes and of the relations of these quantities to the molecular concentrations in the various phases, to the temperature, and to the pressure, enables us, proceeding from the simpler to the more complex cases, to draw conclusions as to the form of the general terms in the above expressions for U, V, Q, and ψ. It is clear that the complete solution of the problem would give us one general form for these "general terms" which would be applicable to *any* phase of *any* molecular composition, at *any* temperature and pressure. It would then be a simple matter to describe *completely* any system of phases given the temperature, pressure, and total masses of the *components.*

We can proceed at first only with relatively simple special cases. On the one hand, the approach to the limiting linear

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[*] This is *not* the case, for instance, in dilute *aqueous* or alcoholic solutions.

[†] The remarkable "gas-analogy" discovered by van't Hoff (and so often mis-used by others) was thus for the first time elucidated,—at least in the case of non-associated simple solvents.

[‡] *Conceivably* also, some special Kinetic Energies (such as kinetic energy of rotation) which *might* depend upon specific intermolecular effects to some extent.

form in "dilute solutions" enables us to learn something of the molecular condition of the solutes, the important first step of all. On the other hand, we have the possibility of using dynamical theory as pointed out above and exemplified in section V.

In the general case, owing to the complexity of the dynamical problem, one may expect that deductions from dynamical theory will be suggestive aids to empirical methods rather than explicit solutions in themselves.

III. A USEFUL MODIFICATION AND SOME EXAMPLES OF APPLICATION.

Though unsuitable for general treatment it is very convenient in many practical cases to use concentrations referred to one molecular species called the "solvent." When such a "solvent" is present in very large excess we have a "dilute solution" of the kind considered by Planck.

If n_0 be the number of molecules of this "solvent," one may express the concentrations as

$$c_1 = \frac{n_1}{n_0}, \quad c_s = \frac{n_s}{n_0}, \quad c_0 = \frac{n_0}{n_0} = 1.$$

It is also a formal convenience to introduce the gas-constant R into the "general terms," writing

$$\mathrm{U} = \Sigma n_s u_s + \mathrm{R} n_0 \Sigma u_x' f_x(c_1 c_2 \ldots .) \quad . \quad . \quad . \quad (22)$$

"Unit quantity of the solution" containing one gram-molecule of the solvent.

c_0 being unity, the general terms now depend only on $c_1 c_2 \ldots$

V being similarly modified it is easily seen that ψ now takes the form

$$\psi = \Sigma n_s\left(\phi_s - \mathrm{R} \log \frac{c_s}{\Sigma c_s}\right) + \mathrm{R} n_0 \Sigma \phi_x' f_x(c_1 c_2 \ldots),$$

or, since c_0 is unity, and using suffix *s* for *solutes*,

$$\psi = n_0[\phi_0 + \mathrm{R} \log (1 + \Sigma c_1)] + \Sigma n_s\left(\phi - \mathrm{R} \log \frac{c_s}{1 + \Sigma c_1}\right)$$
$$+ \mathrm{R} n_0 \Sigma \phi_x' f_x(c_1 c_2 \ldots) \quad . \quad (23)$$

Naturally $\frac{\partial\psi}{\partial n_0}$ is now formally distinguishable from $\frac{\partial\psi}{\partial n_1}$ etc. The general terms in both, however, are somewhat shorter and more easily obtained.

$$\frac{\partial\psi}{\partial n_s} = \phi_s - \mathrm{R}\left[\log c_s - \log (1 + \Sigma c_1) - \Sigma \phi_x' \frac{\partial f_x}{\partial c_s}\right] \quad (24)$$

while

$$\frac{\partial\psi}{\partial n_0}=\phi_0+\mathrm{R}\left\{\log\left(1+\Sigma c_1\right)+\Sigma\phi_x'\left[f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right]\right\}. \quad (25)$$

And similarly

$$\frac{\partial \mathrm{Q}}{\partial n_s}=q_s+\mathrm{R}\Sigma q_x'\frac{\partial f_x}{\partial c_s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\frac{\partial \mathrm{Q}}{\partial n_0}=q_0+\mathrm{R}\Sigma q_x'\left[f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right]. \quad . \quad . \quad . \quad (27)$$

and again

$$\frac{\partial \mathrm{V}}{\partial n_s}=v_s+\mathrm{R}\Sigma v_x'\frac{\partial f_x}{\partial c_s} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$\frac{\partial \mathrm{V}}{\partial n_0}=v_0+\mathrm{R}\Sigma v_x'\left[f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right]. \quad . \quad . \quad . \quad (29)$$

A few illustrations of application may now be given.

We deal generally with two phases (whether naturally or artificially separated) and we may expect the information to be most clear and direct when we keep one phase (the second or (*a*) phase) as simple as possible.

We may place the experimental data under two heads :—

(1) *Concerning the dependence of* $\frac{\partial\psi}{\partial n_0}$ *upon the Concentrations—Solvent-Separation-Data.*

Here we need only consider the common and preferable case, where the second or (*a*) phase consists of pure "solvent" though not necessarily in the same molecular condition as in the first phase. The modifications required when this is not so will be sufficiently obvious and need not be given in these illustrations.

(*a*) *Cryoscopic, Ebullioscopic, Vapour Pressure, and Freezing Pressure* * *Data.* Five important quantities characteristic of the solvent are first accurately determined, viz.:—

(i.) *The two Latent Heats* (L calories per gram) for the two phase-changes of the solvent.

Now
$$\mathrm{L}=\frac{\delta \mathrm{Q}}{\delta \mathrm{M}_0}=\frac{1}{m_0}\frac{\delta \mathrm{Q}}{\delta n_0}$$

for the change $(\delta n_0+\delta n_{0_a})$ in the limit when Σc_1 is zero (pure solvent)—or since by (20),

$$\delta \mathrm{M}=m_0\,\delta n_0+m_{0_a}\,\delta n_{0_a}=0$$

we get
$$\mathrm{L}=\left(\frac{q_{0_a}}{m_{0_a}}-\frac{q_0}{m_0}\right),$$

being an *absorption* of heat on passing *into* the second phase.

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* This method has not so far been used. Its possibilities are being investigated.

Thus by (8)

$$L=T^2\frac{\partial}{\partial T}\left(\frac{\phi_{0_a}}{m_{0_a}}-\frac{\phi_0}{m_0}\right). \quad . \quad . \quad . \quad . \quad . \quad (30)$$

(ii.) The three *Specific volumes* of the three phases of the pure solvent

$$\frac{1}{\rho_0}=\frac{v_0}{m_0}.$$

By (7)

$$\frac{1}{\rho_0}=-T\frac{\partial}{\partial p}\left(\frac{\phi_0}{m_0}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

And similarly

$$\left(\frac{1}{\rho_{0_a}}-\frac{1}{\rho_0}\right)=\frac{\delta V}{\delta M_0}$$

$$=\left(\frac{v_{0_a}}{m_{0_a}}-\frac{v_0}{m_0}\right)=-T\frac{\partial}{\partial p}\left(\frac{\phi_{0_a}}{m_{0_a}}-\frac{\phi_0}{m_0}\right) \quad . \quad . \quad (32)$$

Now for the virtual change $(\delta n_{0_a}+\delta n_0)$ as we have seen

$$-\delta n_{0_a}:\delta n_0=\frac{1}{m_{0_a}}:\frac{1}{m_0}.$$

And by (21) we have for equilibrium between solution in the first phase and pure "solvent" in the second

$$\frac{\phi_{0_a}}{m_{0_a}}-\frac{\phi_0}{m_0}-\frac{R}{m_0}\left\{\log\left(1+\Sigma c_1\right)+\Sigma\phi_x'\left[f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right]\right\}=0 \quad (33)$$

—at temperature T and pressure p.

Making Σc_1 vanish we get *pure "solvent" in both phases*, and the condition for equilibrium at temperature T_0 and pressure p_0 reduces to

$$\frac{\phi_{0_a}}{m_{0_a}}-\frac{\phi_0}{m_0}=0.$$

Clearly therefore $(T-T_0)$ and $(p-p_0)$ being small *,

$$\left\{(T-T_0)\frac{\partial}{\partial T}+(p-p_0)\frac{\partial}{\partial p}\right\}\left\{\frac{\phi_{0_a}}{m_{0_a}}-\frac{\phi_0}{m_0}\right\}$$

$$=\frac{R}{m_0}\left\{\log\left(1+\Sigma c_1\right)+\Sigma\phi_x'\left[f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right]\right\}$$

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* When they are not small the right-hand side of (34) has to be treated as a differential and integrated by means of known equations expressing the physical behaviour of the pure "solvent." Similarly with (35).

—at temperature T and pressure p. That is, by (31) and (33)

$$\frac{\mathrm{R}}{m_0}\left\{\log(1+\Sigma c_1)+\Sigma\phi_x'\left[f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right]\right\}$$

$$=\frac{\mathrm{L}}{\mathrm{T}^2}\Delta\mathrm{T}-\frac{1}{\mathrm{T}}\left(\frac{1}{\rho_{0_a}}-\frac{1}{\rho_0}\right)\Delta p, \qquad (34)$$

where L cals. per gm. is *absorbed* in passing *into* phase (a), $\left(\frac{1}{\rho_{0_a}}-\frac{1}{\rho_0}\right)$c.c./gm. is *dilatation* on passing into phase (a)—and ϕ_1', etc., correspond to temperature T and pressure p.

In Cryoscopic and Ebullioscopic data, Δp is zero.

In Vapour pressure and Freezing pressure data, $\Delta\mathrm{T}$ is zero.

(b) *Osmotic Pressure data.* Here the phases are artificially separated, and maintained *at different pressures*, the "solvent" being in the same molecular condition in both.

Since m_{0_a} and m_0 are the same

$$\delta n_{0_a}=-\delta n_0.$$

For equilibrium of the two phases under different pressures as indicated by the suffixes p and p_0,

$$\left(\frac{\phi_0}{m_0}\right)_{p_0}=\left(\frac{\phi_0}{m_0}\right)_p+\frac{\mathrm{R}}{m_0}\left\{\log(1+\Sigma c_1)+\Sigma\phi_x'\left[f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right]\right\}_p.$$

That is

$$\frac{\mathrm{R}}{m_0}\left\{\log(1+\Sigma c_1)+\Sigma\phi_x'\left[f_x-\Sigma c_1\frac{\partial f_x}{\partial c_1}\right]\right\}_p=\left(\frac{\phi_0}{m_0}\right)_{p_0}-\left(\frac{\phi_0}{m_0}\right)_p$$

$$=-\frac{\partial}{\partial p}\left(\frac{\phi_0}{m_0}\right)\Delta p$$

$$=\frac{v_0}{m_0}\frac{\Delta p}{\mathrm{T}}$$

$$=\frac{\mathrm{P}}{\rho_0\mathrm{T}}, \quad \ldots\ldots\ldots \quad (35)$$

where P (or Δp) is (a small) "osmotic pressure." Now from the form of the expansion of $\log(1+x)$ it is clear that $\log(1+\Sigma c_1)$ approximates to Σc_1 when, and only when, $\frac{1}{2}\Sigma c_1$ is negligible compared with unity. When *in addition* the general terms are negligible we get

$$\frac{\mathrm{P}}{\rho_0\mathrm{T}}=\frac{\mathrm{R}}{m_0}\Sigma c_1$$

or

$$\mathrm{P}\left(\frac{m_0}{\rho_0\Sigma c_1}\right)=\frac{\mathrm{P}v_0}{\Sigma c_1}=\mathrm{RT},$$

which is easily seen to be the "Perfect Gas Law" of van't Hoff, as obtained of course in Planck's simple treatment, but only, as already pointed out, for a simple non-associated "solvent" such as is considered in this section.

(2) *Concerning the dependence of* $\frac{\partial\psi}{\partial n_s}$ *on Concentrations—Solute-Separation-Data.*

For each solute-molecular species we have from (24)

$$\frac{\partial\psi}{\partial n_s}=\phi_s-R\left[\log c_s-\log(1+\Sigma c_1)-\Sigma\phi_x'\frac{\partial f_x}{\partial c_s}\right].$$

We have two main types of data to deal with: (*a*) *Partition data* which includes *solubility data*; (*b*) E.M.F. data in the special case of Electrolytes.

(*a*) For partition data to be of much use the condition and behaviour of the solute considered must be simple (or accurately known) in the second phase.

Thus it may be *alone* in the second phase as in solubility data, or it may form a "perfect solute" in the second phase, *i. e.*,

$$\frac{\partial\psi}{\partial n_{s_a}}=\phi_{s_a}-R\log\frac{c_{s_a}}{1+\Sigma c_{1_a}},$$

as for a constituent of a mixture of perfect gases.

This is the case to a close approximation in the gaseous phase, in dilute solutions of non-electrolytes, and in *non-conducting* dilute solutions of electrolytes. Then for the equilibrium partition,

$$\phi_{s_a}-R\log\frac{c_{s_a}}{1+\Sigma c_{1_a}}=\phi_s-R\left\{\log\frac{c_s}{1+\Sigma c_1}-\Sigma\phi_x'\frac{\partial f_x}{\partial c_s}\right\}$$

i. e., at constant temperature and pressure

$$\Sigma\phi_x'\frac{\partial f_x}{\partial c_s}=\log\frac{c_s}{1+\Sigma c_1}-\log\frac{c_{s_a}}{1+\Sigma c_{1_a}}+\text{Const.}$$

Thus

$$\Delta\left\{\log\frac{c_s}{1+\Sigma c_1}-\log\frac{c_{s_a}}{1+\Sigma c_{1_a}}\right\}=\Delta\Sigma\phi_x'\frac{\partial f_x}{\partial c_s}$$

$$=\Sigma\phi_x'\Delta\frac{\partial f_x}{\partial c_s}. \quad . \quad (36)$$

So that $\Sigma\phi_x'\frac{\partial f_x}{\partial c_s}$ can only be obtained after extrapolation to zero concentration unless $\Delta\frac{\partial f_1}{\partial c_s}$ etc. are already known.

If, however, $\Delta\frac{\partial f_1}{\partial c_s}$ etc. can be reproduced (whether known or not) at different temperatures and pressures, then since by (8)

$$T^2\frac{\partial}{\partial T}\Sigma\phi_x'\Delta\frac{\partial f_x}{\partial c_s}=\Sigma q_x'\Delta\frac{\partial f_x}{\partial c_s}, \quad . \quad . \quad . \quad (37)$$

and by (7)

$$-T\frac{\partial}{\partial p}\Sigma\phi_x'\Delta\frac{\partial f_x}{\partial c_s}=\Sigma v_x'\Delta\frac{\partial f_x}{\partial c_s}, \quad . \quad . \quad . \quad (38)$$

we can thus determine $\Sigma q_x'\Delta\frac{\partial f_x}{\partial c_s}$ and $\Sigma v_x'\Delta\frac{\partial f_x}{\partial c_s}$, and by extrapolation to zero concentration $\Sigma q_x'\frac{\partial f_x}{\partial c_s}$ and $\Sigma v_x'\frac{\partial f_x}{\partial c_s}$. If $\frac{\partial f_1}{\partial c_s}$ etc. or $\Delta\frac{\partial f_1}{\partial c_s}$ etc. be determinable on theoretical grounds we thus obtain q_1' v_1' ϕ_1' etc. at once. Generally, however, it will be possible to determine them by empirical methods given an adequate set of data as to the variation of $\Sigma\phi_x'\frac{\partial f_x}{\partial c_s}$ with concentrations, temperature, and pressure.

In *Solubility Methods* of course $\log\frac{c_{s_a}}{1+\Sigma c_{1_a}}$ vanishes. The modification when the molecular weight of the solute is not the same in the two phases is obvious (*cp.* (33) above).

(b) *E.M.F. Data in the special case of Electrolytes.*—This gives essentially the same information as the partition data, but is more widely and easily applicable. A virtual transference of the solute is effected by means of electrodes, and for this

$$-T\delta\psi=E\delta\epsilon, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

where $\delta\epsilon$ units of electricity are involved in the transference of the δn_1 gm.-mols. of electrolyte or (say) $\nu\delta n_1$ equivalents of electrolyte, so that

$$\delta\epsilon=F\nu\,\delta n_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

F units being one faraday.

Thus if Δ signify the (finite) difference between two phases, (39) and (40) give

$$\begin{aligned}-T\Delta\left(\frac{\partial\psi}{\partial n_1}\right)\delta n_1&=E\delta\epsilon\\&=EF\nu\delta n_1, \quad . \quad . \quad . \quad (41)\end{aligned}$$

i. e.
$$\frac{E}{T} = -\frac{1}{F\nu}\Delta\left(\frac{\partial\psi}{\partial n_1}\right), \quad . \quad . \quad . \quad . \quad (42)$$

$$T^2\frac{\partial}{\partial T}\left(\frac{E}{T}\right) = -\frac{1}{F\nu}\Delta\left(\frac{\partial Q}{\partial n_1}\right). \quad . \quad . \quad . \quad (43)$$

$$T\frac{\partial}{\partial p}\left(\frac{E}{T}\right) = \frac{1}{F\nu}\Delta\left(\frac{\partial V}{\partial n_1}\right). \quad . \quad . \quad . \quad . \quad (44)$$

Now when we consider that, when the solvent is the same in both phases,

$$\Delta\frac{\partial\psi}{\partial n_s} = -R\Delta\left\{\log c_s - \log\left(1+\Sigma c_1\right) - \Sigma\phi_x'\frac{\partial f_x}{\partial c_s}\right\}, \quad (45)$$

$$\Delta\frac{\partial Q}{\partial n_s} = R\Delta\Sigma q_x'\frac{\partial f_x}{\partial c_s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

$$\Delta\frac{\partial V}{\partial n_s} = R\Delta\Sigma v_x'\frac{\partial f_x}{\partial c_s}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

it immediately becomes clear that the measurement of E/T and its temperature and pressure coefficients for concentration cells in which the molecular concentrations are known gives us *precisely the same information as the partition data* already discussed. But (within its obvious limitations) the E.M.F. method is much more easily and widely applicable.

IV. Polymerized and Mixed Solvents.

Hitherto, like Planck, we have assumed a complete knowledge of the molecular constitution of the solution. In the case of an absolutely non-associated solvent such as a paraffin this will be readily obtainable, but *many of our best solvents* consist of two or three different kinds of molecules in proportions of which we have no more than a rough idea.

Concentrations referred to the "number of molecules of solvent" as denominator, are obviously of no practical use to us in these cases, for indeed our definition of the "solvent" as a particular molecular species has here to be altered to "a particular *group* of molecular species, *incompletely specified*."

We have, therefore, to consider carefully how far both Planck's treatment of extreme dilutions and the above treatment of the general case can be made practically applicable—by suitable modification—in the face of this deficiency of data.

Now in "Solvent-Separation-data," we separate, in the cases we are now considering, not *one* molecular species but all those constituting the "solvent," and *in the proportions in which they occur.* This applies also to the use of *mixed* solvents—of which the molecular constitution may or may not be known.

We shall now obtain a general modification of the method of the preceding sections, suitable for these special cases, and which will show how far we can go with limited knowledge of the molecular constitution of the solvent.

We begin by referring the molecular concentrations to the *mass* M_0 of the solvent, which, incidentally, brings us into closer touch with experimental practice.

$$c_{01} = \frac{n_{01}}{M_0}, \quad c_1 = \frac{n_1}{M_0}, \quad M_0 = \Sigma n_{01} m_{01},$$

where $m_{01}\ m_{02}\ldots$ are the molecular weights (in grams) of the various molecular species constituting the "solvent," and

$$\frac{\partial M_0}{\partial n_{01}} = m_{01}, \quad \frac{\partial M_0}{\partial n_{02}} = m_{02}, \text{ etc.}$$

The *mean* molecular weight $\dfrac{M_0}{\Sigma n_{01}}$ or $\dfrac{1}{\Sigma c_{01}}$ may be written $\overline{m}_0$.

At first, let us assume that the molecular constitution of the solvent is *independent of the concentrations* $c_1\ c_2\ldots$ of the *solutes*. Then $c_{01}\ c_{02}\ldots$ can only depend on temperature and pressure, are not differentiable with respect to $c_1 c_2\ldots$, and, in the general terms, can therefore be relegated entirely to the parameters $u_1'\ u_2'\ldots$ and $v_1'\ v_2'\ldots$.

Taking now as "unit quantity of solution," the amount containing one gram of solvent, we have

$$U = \Sigma n_{01} u_{01} + \Sigma n_1 u_1 + RM_0 \Sigma u_x' f_x(c_1 c_2 \ldots), \quad (48)$$

$$V = \Sigma n_{01} v_{01} + \Sigma n_1 v_1 + RM_0 \Sigma v_x' f_x(c_1 c_2 \ldots). \quad (49)$$

Whence clearly, as in preceding cases,

$$\psi = \Sigma n_{01}\left(\phi_{01} - R \log \frac{c_{01}}{\Sigma c}\right) + \Sigma n_1\left(\phi_1 - R \log \frac{c_1}{\Sigma c}\right)$$
$$+ RM_0 \Sigma \phi_x' f_x (c_1\ c_2 \ldots) \quad (50)$$

But

$$\Sigma c = \Sigma c_{01} + \Sigma c_1 = \frac{1}{\overline{m}_0} + \Sigma c_1 = \frac{1}{\overline{m}_0}(1 + \overline{m}_0 \Sigma c_1),$$

so that

$$\begin{aligned}\psi = M_0\Big[\Sigma c_{0_1}\phi_{0_1} - R\Sigma c_{0_1}\log \bar{m}_0 c_{0_1} + \frac{R}{\bar{m}_0}\log\,(1+\bar{m}_0\Sigma c_1)\Big] \\ + \Sigma n_1[\phi_1 - R\log \bar{m}_0\, c_1 + R\log\,(1+\bar{m}_0\Sigma c_1)] \\ + RM_0\Sigma\phi_x' f_x(c_1 c_2 \ldots) \quad . \quad . \quad . \quad (51)\end{aligned}$$

We have assumed $\bar{m}_0$, c_{0_1} c_{0_2} . . . to be dependent only on temperature and pressure, so that we can include $-R\log\bar{m}_0$ under the symbols ϕ_1 ϕ_2 etc., and we can write ϕ_M for the quantity Σc_{0_1} $(\phi_{0_1} - R\log\bar{m}_0\, c_{0_1})$ getting

$$\begin{aligned}\psi = M_0\Big[\phi_M + \frac{R}{\bar{m}_0}\log\,(1+\bar{m}_0\Sigma c_1)\Big] \\ + \Sigma n_1\Big[\phi_1 - R\Big\{\log c_1 - \log\,(1+\bar{m}_0\Sigma c_1)\Big\}\Big] \\ + RM_0\Sigma\phi_x' f_x(c_1 c_2 \ldots) . \quad . \quad . \quad (52)\end{aligned}$$

Thence we have

$$\left.\begin{aligned}\frac{\partial\psi}{\partial M_0} = \phi_M + \frac{R}{\bar{m}_0}\log\,(1+\bar{m}_0\Sigma c_1) + R\Sigma\phi_x'\Big[f_x - \Sigma c_1\frac{\partial f_x}{\partial c_1}\Big] \\ \text{and} \qquad\qquad\qquad\qquad \\ \frac{\partial\psi}{\partial n_s} = \phi_s - R\Big\{\log c_s - \log\,(1+\bar{m}_0\Sigma c_1) - \Sigma\phi_x'\frac{\partial f_x}{\partial c_s}\Big\}\end{aligned}\right\} (53)$$

We have treated $\bar{m}_0$, c_{0_1} c_{0_2}, ..., as dependent only on temperature and pressure.

In a solvent which is a mixture of inert non-associated liquids these quantities will clearly be independent even of temperature and pressure. The modification just given will of course apply and be useful here, but might be dispensed with since the exact molecular constitution of such a solvent could readily be determined. In a polymerized solvent $\bar{m}_0$ c_{0_1} c_{0_2} . . . . depend on the chemical equilibrium between the different molecules of the solvent, which *in the general case* cannot be assumed to be entirely independent of c_1 c_2 . . . . In the general case then, ϕ_M ϕ_1 ϕ_1' etc. in (52) will be differentiable with respect to c_1 c_2 . . ., and (53) *et seq.* will not be valid.

We have to consider the order of magnitude of the effect of the variations of c_1 c_2 . . . . upon the values of the quantities $\frac{\partial\psi}{\partial n_s}$ and $\frac{\partial\psi}{\partial M_0}$.

In the first place, we note that variations in c_1 c_2 . . . .

will affect the quantities c_{01} c_{02} etc. only indirectly and relatively slightly, or in other words will produce only second-order variations in c_{01} c_{02} . . . . .

In the second place, since $\Sigma\, m_{01}\, c_{01}$ is constant (unity), it is clear on examining (51) that the effects upon ψ of variations of c_{01} c_{02} . . . . are throughout more or less mutually compensatory.

In the case of $\Sigma c_{01} \log \overline{m}_0\, c_{01}$, for instance, we note that the mutual compensation will be greatest when c_{01} c_{02} . . . are of similar order. When, however, this is far from the case, and any of them, c_{01} (say) approaches either of the extremes zero or $1/\overline{m}_0$, then, since the relative magnitude of the effect on ψ of a variation in c_{01} may be estimated as

$$\frac{\partial}{\partial \log c_{01}}[c_{01} \log \overline{m}_0\, c_{01}] = c_{01}\,[\log \overline{m}_0\, c_{01} + 1],$$

we see that this is small whether c_{01} approaches zero or $1/\overline{m}_0$.

Finally, the "general terms" (which may depend somewhat on c_{01}, c_{02} . . . .) are themselves small when c_1 c_2 . . . . are not large, so that altogether it is clear that the effects upon ψ of variations in c_{01}, c_{02} . . . . are relatively small, that is, second-order effects.

That is, variations in c_1, c_2 . . . . will produce only third-order variations in ψ.

From the general form of this argument we must expect of course that special cases will be producible in which it does not hold, but, in general, we are able to conclude that it is possible by means of the modification given in this section to go a surprisingly long way without complete knowledge of the molecular constitution of the solvent.

Naturally the most general case will require *complete* knowledge of the constitution of the phase for accurate treatment, but even then the grouping of equation (51) may be found convenient, concentrations being referred to the mass of the whole "solvent," rather than to the numerical quantity of one molecular form of the "solvent." The derivatives $\frac{\partial\psi}{\partial M_0}$ and $\frac{\partial\psi}{\partial n_s}$ obtainable from (51) are of course obvious.

Returning to the equations (53) we see that they depend on $\overline{m}_0$ in respect of the term $\log(1+\overline{m}_0\Sigma c_1)$.

Expanded, this term takes the form

$$\overline{m}_0\Sigma c_1[1-\tfrac{1}{2}\overline{m}_0\Sigma c_1+\ldots\ldots].$$

As a *first* approximation we may neglect all but the first term of this series, and in $\frac{\partial\psi}{\partial n_s}$ clearly we may neglect even the first term in comparison with $\log c_s$. Thus we obtain the equations

$$\psi = \mathrm{M}_0(\phi_\mathrm{M} + \mathrm{R}\Sigma c_1) + \Sigma n_1(\phi_1 - \mathrm{R}\log c_1) + \mathrm{RM}_0\Sigma\phi_x' f_x(c_1 c_2 \ldots) \quad . \; . \; . \; (54)$$

and thence

$$\left.\begin{aligned} \frac{\partial\psi}{\partial \mathrm{M}_0} &= \phi_\mathrm{M} + \mathrm{R}\left\{\Sigma c_1 + \Sigma\phi_x'\left(f_x - \Sigma c_1\frac{\partial f_x}{\partial c_1}\right)\right\} \\ \frac{\partial\psi}{\partial n_s} &= \phi_s \; - \mathrm{R}\left\{\log c_s - \Sigma\phi_x'\frac{\partial f_x}{\partial c_1}\right\} \end{aligned}\right\}, \qquad (55)$$

—from which $\overline{m}_0$ is completely eliminated so that no knowledge of the constitution of the solvent is assumed.

In this first approximation we have neglected $\frac{1}{2}\overline{m}_0\Sigma c_1$ in comparison with unity.

Now, for example, taking $\overline{m}_0$ for water as roughly 36, we see that in half-molar solution the error involved in this first approximation is about one per cent.

It is clear that at or above tenth-molar concentration we ought to proceed to a further degree of approximation by including in $\frac{\partial\psi}{\partial n_s}$ the *first* term and in $\frac{\partial\psi}{\partial \mathrm{M}_0}$ the *second* term of the expansion of $\log(1+\overline{m}_0\Sigma c_1)$. We thus get the equations

$$\left.\begin{aligned} \frac{\partial\psi}{\partial \mathrm{M}_0} &= \phi_\mathrm{M} + \mathrm{R}\left\{\Sigma c_1(1 - \tfrac{1}{2}\overline{m}_0\Sigma c_1) + \Sigma\phi_x'\left[f_x - \Sigma c_1\frac{\partial f_x}{\partial c_1}\right]\right\} \\ \frac{\partial\psi}{\partial n_s} &= \phi_s \; - \mathrm{R}\left\{\log c_s - \overline{m}_0\Sigma c_1 - \Sigma\phi_x'\frac{\partial f_x}{\partial c_s}\right\}, \end{aligned}\right\} \quad . \; . \; . \; (56)$$

in which, it is seen, $\overline{m}_0$ only enters in the form of small correction terms, so that, until considerable concentrations are reached, a quite approximate idea of $\overline{m}_0$ will suffice.

These equations (56) may profitably be substituted for equations (55) at and above tenth-molar concentration. Whether the inclusion of a further term of the expansion of $\log(1+\overline{m}_0\Sigma c_1)$ would be of any value (except possibly in certain special cases) is very doubtful, particularly when, as in this section, we are considering associated or polymerized solvents, for at really considerable concentrations the third-order effects already discussed will generally enter and invalidate equations (53).

Appendix to Section IV.

Non-validity of "Mass-Action Equations" for Perfect Solutes.

It has been common to use equations of the form of (55) with the "general terms" omitted, or rather the equivalents thereof, as the criteria of a "perfect solute."

It may be suggested that this is incorrect, not being in accord with the obviously rational definition of a perfect solute as a solute which behaves like a constituent of a mixture of perfect gases,—a solute, in fact, which does not affect the "general terms" but only the linear, and for which

$$\frac{\partial\psi}{\partial n_s}=\phi_s-\mathrm{R}[\log c_s-\log(1+\overline{m}_0\Sigma c_1)]. \quad . \quad . \quad (57)$$

Now at very low concentrations (57) approximates closely to

$$\frac{\partial\psi}{\partial n_s}=\phi_s-\mathrm{R}\log c_s, \quad . \quad . \quad . \quad . \quad . \quad (58)$$

and (58), or something equivalent to it, has hitherto generally been the criterion of a perfect solute.

The question arises, as an interesting example of what has been said with regard to the "second approximation" (56), whether cases may not easily arise in which a solute remains "perfect" in accordance with the true criterion (57), within the error of experiment even at concentrations for which (57) does *not*, within the experimental error, approximate to equation (58).

We have seen that in aqueous solution when Σc_1 is half-molar concentration the value of $\log(1+\overline{m}_0\Sigma c_1)$ is of the order of ·02.

Now consider a chemical reaction between solutes which are "perfect" in accordance with the true criterion (57).

We have from (21) for equilibrium with regard to the virtual change $\Sigma\delta n_s$

$$\delta\psi=0,$$

that is

$$\Sigma\frac{\partial\psi}{\partial n_s}\,.\,\delta n_s=0.$$

Or if the lowest possible integers $\nu_1, \nu_2, \ldots$ be chosen so that

$$\delta n_1 : \delta n_2 : \delta n_3 : \ldots\ldots = \nu_1 : \nu_2 : \nu_3 : \ldots\ldots$$

we obtain, (for perfect solutes) from (57)

$$\Sigma\nu_s\{\phi_s - \mathrm{R}[\log c_s - \log(1+\overline{m}_0\Sigma c_1)]\} = 0,$$

whence

$$\Sigma\nu_s \log c_s - (\Sigma\nu_s)\log(1+\overline{m}_0\Sigma c_1) = \frac{1}{\mathrm{R}}\Sigma\nu_s\phi_s$$

$$= \log \mathrm{K}, \quad . \quad . \quad . \quad (59)$$

whereas the ordinary "mass-action equation" has been

$$\Sigma\nu_s \log c_s \qquad = \log \mathrm{K}'. \quad . \quad . \quad . \quad . \quad . \quad (60)$$

We see therefore that

$$\log \mathrm{K}' = \log \mathrm{K} + (\Sigma\nu_s)\log(1+\overline{m}_0\Sigma c_1) \quad . \quad . \quad (61)$$

or

$$\mathrm{K}' = \mathrm{K}(1+\overline{m}_0\Sigma c_1)^{\Sigma\nu_s}, \quad . \quad . \quad . \quad . \quad (62)$$

or as long as $\overline{m}_0\Sigma c_1$ is small

$$\mathrm{K}' = \mathrm{K}(1+\overline{m}_0\Sigma c_1\Sigma\nu_s). \quad . \quad . \quad . \quad . \quad (63)$$

We thus find that, except when $\Sigma\nu_s$ is zero, the equilibrium constant as hitherto written down should depend linearly upon the *total* concentration of solutes present (whether taking part in the reaction or not) if the participants in the reaction are behaving as perfect solutes.

The magnitude of the *relative* variation of K′ is seen to depend upon the magnitude of $\overline{m}_0\Sigma c_1\Sigma\nu_s$ compared with unity.

Now supposing for simplicity that the probable relative error in the experimental determination of each of the concentrations c_s is uniformly equal to x, then the "probable error" in K′ is of course

$$x\Sigma[\nu_s],$$

so the possibility of detecting the variation which we are expecting in K′ depends on the magnitude of

$$\frac{\Sigma\nu_s}{\Sigma[\nu_s]} \cdot \frac{\overline{m}_0\Sigma c_1}{x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (64)$$

Since, as we have seen, for molar aqueous solution $\overline{m}_0\Sigma c_1$ is probably at least ·04, we find that evidence of the variation we are considering will, in easily chosen cases, become decisive as soon as the experimental error is reduced much below one per cent.

It is to be noted that Σc_1 represents the range of variation of the total concentration of solutes present, not of the concentrations of the reactants, which latter alone, however, are required to behave as perfect solutes.

There seems, therefore, good reason to believe that in a few well-chosen cases this effect might be demonstrated beyond doubt, and the quantity $\overline{m}_0$ found with some approximation in each case. Agreement between the several values of $\overline{m}_0$ thus found would justify some confidence in this *estimate of the mean molecular weight of the solvent.*

It seems probable, however, that measurements of the solubility of a moderately soluble gas would be the most hopeful first approach to this investigation,—the theoretical treatment being perfectly obvious from what has gone before. Experimental investigation of this question is contemplated.

V. A SPECIAL APPLICATION. THE THEORY OF ELECTROLYTES.

It was pointed out in section II. that the "molecular" treatment of thermodynamics opens up the way for the use of dynamical theory. The calculation of the general energy terms will be complex, however, in the general case and only rough ideas and indications may be obtainable at first.

The idea put forward by Sutherland in 1902, that strong electrolytes are completely ionized, at any rate in dilute solution, is of great interest in this connexion.

For in a solution of ions we have forces at work which are amenable to relatively simple dynamical treatment, and which are considerable in dilute solutions where other inter-solute forces are negligible.

The credit of first showing that this is so is undoubtedly due to Milner *, and the full value of Milner's calculation of what he calls the "Virial" of a mixture of ions has perhaps scarcely been realized. Milner calculated $\Sigma\Sigma r\phi(r)$, the sum of all the electrostatic forces $\phi(r)$ in a chaos of equal numbers of oppositely charged massive points, each force being multiplied by the distance (r) over which it acts.

Calling this the "virial" of a mixture of ions he proceeds to apply to the osmotic pressure of a solution of ions the Virial theorem established by Clausius for a gas. He points out † that because the law of force is that of the inverse

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* Phil. Mag. ser. 6, xxiii. p. 551; xxv. p. 742.

† *Loc. cit.* xxv. p. 747.

square, this "virial" represents also the *potential energy* of all the electrostatic forces.

Milner then gives a thermodynamic demonstration[*] supporting his application of the Virial theorem "to the complex phenomenon which the osmotic pressure of an electrolyte undoubtedly is." But this demonstration is open to grave doubts, for it depends on treating the solute thermodynamically as an independent system, whose "external pressure" is the osmotic pressure of the solution, and also on regarding K, the dielectric constant of the medium, as independent of temperature.

Of course, neither of these can possibly be strictly permissible, but also one cannot, *à priori*, assume even approximate validity as regards the conclusions to which they may lead.

Using the general molecular-thermodynamic method developed in this paper, we shall, by means of a simple example, reach the conclusion that this application of the Virial theorem cannot be, in any general sense, valid.

The Non-validity of the "Virial" Equation for Osmotic Pressure.

Consider a solution of a binary electrolyte, containing c gram-molecules of electrolyte per gram of solvent.

Suppose the "virial" per gram-molecule of electrolyte to be given by

$$\mathrm{R}u'c^{\frac{1}{3}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (65)$$

where u' is independent of c.

Then c being $\frac{n}{\mathrm{M}_0}$ we have

$$\begin{aligned}\mathrm{U}&=\mathrm{M}_0u_0+2nu-n\mathrm{R}u'c^{\frac{1}{3}}\\&=\mathrm{M}_0u_0+2nu-\mathrm{R}\mathrm{M}_0u'c^{\frac{4}{3}}, \quad . \quad . \quad . \quad . \qquad (66)\end{aligned}$$

where u is a mean value for the two ions[†].

Assuming, further, that owing to the smallness of the external pressure the general terms in V can be neglected in comparison with that in U, we shall write

$$\mathrm{V}=\mathrm{M}_0v_0+2nv, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (67)$$

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[*] *Loc. cit.* xxv. p. 748.

[†] The discussion of the possibility of distinguishing the thermodynamic properties of the complementary ions of an electrolyte is reserved for a later paper.

and then obviously for dilute solution [*cf.* (55)] we shall obtain

$$\psi = \mathrm{M}_0[\phi_\mathrm{M} + 2\mathrm{R}c] + 2n(\phi - \mathrm{R}\log c) - \mathrm{R}\mathrm{M}_0\phi' c^{\frac{4}{3}}, \tag{68}$$

where

$$\phi' = \mathrm{K}' - \frac{u'}{\mathrm{T}} + \int \frac{du'}{\mathrm{T}}$$

and

$$\frac{\partial \phi'}{\partial \mathrm{T}} = \frac{u'}{\mathrm{T}^2}, \quad . \; . \; . \; . \; . \; . \; . \tag{69}$$

or

$$\frac{\partial}{\partial \mathrm{T}}(\phi'\mathrm{T}) = \phi' + \frac{u'}{\mathrm{T}} = \mathrm{K}' + \int \frac{du'}{\mathrm{T}} \quad . \; . \; . \; . \tag{70}$$

From (68) we derive

$$\frac{\partial \psi}{\partial \mathrm{M}_0} = \phi_\mathrm{M} + 2\mathrm{R}c + \tfrac{1}{3}\mathrm{R}\phi' c^{\frac{4}{3}},$$

so that for a small osmotic pressure P [*cf.* (35)]

$$\frac{\mathrm{P}}{\mathrm{RT}\rho_0 c} = 2 + \tfrac{1}{3}\phi' c^{\frac{1}{3}}. \quad . \; . \; . \; . \; . \; . \tag{71}$$

Now Milner, applying his thermodynamic demonstration, with the form of "virial" we have assumed would obtain

$$\frac{\mathrm{P}}{\mathrm{RT}\rho_0 c} = 2 - \tfrac{1}{3}\frac{u'}{\mathrm{T}} c^{\frac{1}{3}} \quad . \; . \; . \; . \; . \; . \; . \tag{72}$$

Comparing (71) and (72) we see that this would mean

$$\phi' + \frac{u'}{\mathrm{T}} = 0, \quad . \; . \; . \; . \; . \; . \; . \tag{73}$$

i. e., by (70),

$$\frac{\partial}{\partial \mathrm{T}}(\phi'\mathrm{T}) = 0, \quad . \; . \; . \; . \; . \; . \; . \tag{74}$$

i. e., by (73),

$$\frac{\partial}{\partial \mathrm{T}}(u') = 0. \quad . \; . \; . \; . \; . \; . \; . \tag{75}$$

Now Milner's thermodynamic demonstration will apply to the form (65) if $u'/\rho_0^{\frac{1}{3}}$ is independent of temperature, *i. e.* if:

$$\frac{\partial}{\partial \mathrm{T}}\left(\frac{u'}{\rho_0^{\frac{1}{3}}}\right) = 0,$$

so that rigorous thermodynamics roughly bears out his demonstration in this simplest case, making nearly the same demand in order to arrive at the "virial" equation. But comparing (70) and (74) we see that this requirement involves also that

$$\left[\mathrm{K}'+\int\frac{du'}{\mathrm{T}}\right]=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (76)$$

as in the hypothetical perfect gaseous state (extremely hot and rarefied) conceived for the determination of the integration constants in the entropy function (see section I.).

This reveals the impossibility of *even an approximate* fulfilment of the above requirement, such as might rashly be assumed on the grounds that $\frac{\partial u'}{\partial \mathrm{T}}$ (in (75)) will probably not be large.

For consider firstly that u' depends directly on the Dielectric-constant of the solvent, which would suffer an enormous total change during this transition to the gaseous state, and secondly that since c is n/M_0, u' depends also on ρ_0 the density of the solvent, whose variation (total) is perhaps even more obvious.

It is clear that if the validity of the general method of this paper is conceded, Milner's use of the Virial theorem cannot possibly be justified on theoretical grounds.

But if we thus reject his application of the Virial theorem, the *true value of Milner's calculation of* $\Sigma\Sigma r\phi(r)$ *is in no way diminished*, as the opening of this section will have indicated.

The Application of Milner's Calculation.

As he fully realizes, Milner's assumptions limit him to fairly dilute solution where, in addition to the satisfaction of certain requirements involved in the probability considerations, the ions may be regarded as point charges, and the solvent is present in such large excess that its dielectric constant K may be used with accuracy in calculating the forces between the ions.

But Milner states in a footnote [*] that, involved in the calculation of $\Sigma\Sigma r\phi(r)$ is the implicit assumption that K is independent of the temperature, saying that "if it were not constant, the electrical force between two ions would depend on their kinetic energies as well as on their positions."

There appears to be some mistake here.

The electrostatic force between two ions will depend on the effective dielectric constant of the intervening medium. In dilute solution—to which Milner is limited—the large majority of the ions will be separated by many molecules of solvent, so that, on the average, the effective dielectric

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[*] *Loc. cit.* xxv. p. 748.

constant will be that of the pure solvent, corresponding to the statistical temperature. In centinormal aqueous solution of KCl, for instance, there are about 3000 solvent molecules ("dihydrol") to every molecule of electrolyte.

But quite apart from this, it is far from clear how the kinetic energies of particular ions can enter into the question of the electrostatic forces in which those particular ions are concerned. The logical force of the above quotation does not seem at all obvious.

Thus Milner's calculation of $\Sigma\Sigma r\phi(r)$ appears to rest on a stricter basis than he himself has claimed, though his application of it in the form of the Virial theorem seems altogether doubtful theoretically.

The calculation proved to be complex, and the form in which the final approximation was cast

$$\mathrm{RT}h\phi(h)$$

depends on a tabulated function $\phi(h)$.

In an inconspicuous footnote *, Milner remarks that "It may be shown as an approximation, and when h is very small" that

$$\phi(h)=-\sqrt{\tfrac{3}{2}\pi h}. \quad . \quad . \quad . \quad . \quad . \qquad (77)$$

Now in dilute conducting solutions h *is* small, and owing to the rather striking result to which it will lead, one is very interested to find, on examining the values for $\frac{1}{3}h\phi(h)$ given by Milner in the later paper, that up to centinormal (or even higher concentrations) we shall not be very far out in applying this approximation (77), which, since h is of the form $\mathrm{A}'c^{\frac{1}{3}}$, means that $\Sigma\Sigma r\phi(r)$ is of the form

$$\mathrm{A}c^{\frac{1}{2}} \text{ per gram-molecule.} \quad . \quad . \quad . \quad . \quad . \qquad (78)$$

This gives for the general energy term

$$n\mathrm{R}u'c^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (79)$$

instead of the expression $n\mathrm{R}u'c^{\frac{1}{3}}$ used in (66), and we shall obviously obtain

$$\psi=\mathrm{M}_0(\phi_{\mathrm{M}}+2\mathrm{R}c)+2n(\phi-\mathrm{R}\log c)-\mathrm{RM}_0\phi' c^{\frac{3}{2}}, \quad . \qquad (80)$$

whence

$$\left.\begin{aligned}\frac{\partial\psi}{\partial\mathrm{M}_0}&=\phi_{\mathrm{M}}+\mathrm{R}\{2c+\tfrac{1}{2}\phi' c^{\frac{3}{2}}\}\\ \frac{\partial\psi}{\partial n}&=2\{\phi-\mathrm{R}(\log c+\tfrac{3}{4}\phi' c)^{\frac{1}{2}}\}\end{aligned}\right\}, \quad . \quad . \qquad (81)$$

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* *Loc. cit.* xxiii. p. 575.

and for solvent-separation data [*cf.* (35) and (34)]

$$\frac{P}{RT\rho_0 c} = \frac{L\Delta T}{RT^2 c} - \left(\frac{1}{\rho_{0_a}} - \frac{1}{\rho_0}\right)\frac{\Delta p}{RTc} = 2 + \tfrac{1}{2}\phi' c^{\frac{1}{2}} = i. \quad . \qquad (82)$$

Now in the nomenclature of G. N. Lewis, as will be clear from (42), we could write

$$\frac{\partial \psi}{\partial n} = 2\{(\text{const.}) - R \log c\gamma\} \quad . \quad . \quad . \quad . \qquad (83)$$

for a completely ionized electrolyte, this being simply the equivalent of Lewis's definition of γ in this case, and γ being what Brönsted calls the "stoichiometric activity coefficient" of an ion.

Comparing (81) and (83) we find

$$\log \gamma = \tfrac{3}{4}\phi' c^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (84)$$

But Lewis and Linhart* have recently shown as a purely empirical fact derived from the most accurate data then available, that this form $Bc^{\frac{1}{2}}$ is actually the limiting form of $\log \gamma$ for uni-univalent strong electrolytes in very dilute solution $\left(\text{below } \frac{N}{100}\right)$. This seems to be rather striking confirmation both for Milner's calculation of $\Sigma\Sigma r\phi(r)$ and for the "complete ionization" theory.

It will be very interesting to test Milner's calculation more closely by obtaining the experimental value for u' itself.

If (and only if), as we have assumed, the general terms in the expression for V can be neglected in comparison with those in U †, then, as we have seen [equation (69)]

$$\frac{\partial \phi'}{\partial T} = \frac{u'}{T^2},$$

that is, at a given concentration (c) by (82)

$$\frac{\partial}{\partial T}(i) = \tfrac{1}{2}c^{\frac{1}{2}} \cdot \frac{u'}{T^2}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (85)$$

and by (84)

$$\frac{\partial}{\partial T} \cdot \log \gamma = \tfrac{3}{4}c^{\frac{1}{2}} \cdot \frac{u'}{T^2}; \quad . \quad . \quad . \quad . \quad . \quad . \qquad (86)$$

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* Journ. Amer. Chem. Soc. xli. p. 1951 (1919).

† This assumption requires that the pressure coefficient of $\log \gamma$, when multiplied by $\frac{p}{T}$, be negligible in comparison with the temperature coefficient of $\log \gamma$, and of this there can be little doubt.

so that accurate data, whether solvent-separation data or solute-separation data, for low concentrations $\left(\text{below } \frac{N}{100}\right)$ at different temperatures would enable us to calculate u', and compare the experimental value with the theoretical value calculated by Milner from dynamical theory.

Mixtures of Strong Electrolytes.

It will be of interest, now, to consider the extension of this theory of electrolytes to the more general case of a *mixture* of strong electrolytes, particularly as experimental data on this head are forthcoming.

Consider a very dilute solution of various univalent ions, in total number Σn_1, and in total concentration Σc_1. These quantities correspond to $2n$ and to $2c$ respectively in the simple case of a single electrolyte.

In such a solution we may regard all the ions as point-charges, and (as we have seen, in that case) express the total $\Sigma\Sigma r\phi(r)$, (*cf.* (79), as

$$(\tfrac{1}{2}\Sigma n_1)\,\mathrm{R}u'(\tfrac{1}{2}\Sigma c_1)^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad . \quad (87)$$

We may conveniently write

$$\tfrac{1}{2}\Sigma c_1 = \mathrm{C}_i, \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

the total equivalent concentration, or total concentration of ions of one sign, so that

$$\frac{\partial}{\partial c_1}(\mathrm{C}_i) = \tfrac{1}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (89)$$

And, neglecting again the general volume terms, we have

$$\mathrm{U} = \mathrm{M}_0 u_0 + \Sigma n_1 u_1 - \mathrm{RM}_0 u' \mathrm{C}_i^{\frac{3}{2}}, \quad . \quad . \quad . \quad (90)$$

$$\mathrm{V} = \mathrm{M}_0 v_0 + \Sigma n_1 v_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

so that

$$\psi = \mathrm{M}_0(\phi_{\mathrm{M}} + 2\mathrm{RC}_i) + \Sigma n_1(\phi_1 - \mathrm{R}\log c_1) - \mathrm{RM}_0\phi'\mathrm{C}_i^{\frac{3}{2}}, \quad (92)$$

and thence

$$\left.\begin{aligned} \frac{\partial\psi}{\partial \mathrm{M}_0} &= \phi_{\mathrm{M}} + \mathrm{RC}_i\{2 + \tfrac{1}{2}\phi'\mathrm{C}_i^{\frac{1}{2}}\} \\ \frac{\partial\psi}{\partial n_s} &= \phi_s - \mathrm{R}\{\log c_s + \tfrac{3}{4}\phi'\mathrm{C}_i^{\frac{1}{2}}\} \end{aligned}\right\}, \quad . \quad . \quad (93)$$

that is

$$i = 2 + \tfrac{1}{2}\phi'\mathrm{C}_i^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad (94)$$

$$\log\gamma_s = \tfrac{3}{4}\phi'\mathrm{C}_i^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (95)$$

This means that the thermodynamic behaviour of all the ions in the same solution of (entirely univalent) ions is the same and depends only on the total equivalent concentration C_i.

Now this is precisely what has been deduced in recent years as a purely empirical rule by Lewis, Loomis, Harned, Ming Chow, and others *.

It is a very significant fact that these workers have shown this rule to hold quite closely at concentrations much higher than are contemplated in the above. Thus, probably we shall be close to the truth in regarding $\Sigma\Sigma r\phi(r)$ as a function of C_i, even at these somewhat higher concentrations where it does not take the simple form $Ru'C_i^{\frac{3}{2}}$.

For tentative preliminary treatment of the higher concentrations, the use of the general form

$$R\Sigma u_1'C_i^{m_1+1} \quad \ldots\ldots \quad (96)$$

may be suggested, being fairly elastic since m_1, m_2, ... can have any positive values, and possessing the advantage of being easy to work with since it gives

$$U=M_0u_0+\Sigma n_1u_1-RM_C\Sigma u_1'C_i^{m_1+1}, \quad \ldots\ldots \quad (97)$$

$$\psi=M_0(\phi_M+2RC_i)+\Sigma n_1(\phi_1-R\log c_1)-RM_0\Sigma\phi_1'C_i^{m_1+1}, \quad \ldots \quad (98)$$

and

$$\frac{\partial\psi}{\partial M_0}=\phi_M+RC_i\left\{2+\Sigma m_1\phi_1'C_i^{m_1}\right\}, \quad \ldots \quad (99)$$

$$\frac{\partial\psi}{\partial n_s}=\phi_s-R\left\{\log c_s+\Sigma\frac{m_1+1}{2}\phi_1'C_i^{m_1}\right\}. \quad (100)$$

That is

$$i=2+\Sigma m_1\phi_1'C_i^{m_1}, \quad \ldots\ldots \quad (101)$$

$$\log\gamma=\Sigma\frac{m_1+1}{2}\phi_1'C_i^{m_1}. \quad \ldots\ldots \quad (102)$$

On the basis of Milner's calculation the first m would be $\frac{1}{2}$, and the rest higher than $\frac{1}{2}$, so that (94) and (95) would be the limits of (101) and (102), as found by Lewis and Linhart.

For bivalent binary electrolytes one would expect the same form of virial with a different limiting parameter B.

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* Journ. Amer. Chem. Soc. xxxi. p. 335 (1909); xxxviii. p. 1986 (1916). xxxviii. p. 2356 (1916); xxxix. p. 1138 (1917). xxxvi. p. 632 (1911); xlii. p. 488 (1920). xxxvii. p. 2460 (1915).

If the limiting form has really been reached by Lewis and Linhart in the few such cases investigated, this expectation would not appear to have been realized, but the data can scarcely be regarded as very satisfactory.

Owing to the electrostatic forces being four times as great in this case, we should expect the limiting form to be attained only at much greater dilution than in the case of univalent binary electrolytes.

Now when we consider a mixture of ions of different valencies, the corresponding calculation of $\Sigma\Sigma r\phi(r)$ becomes somewhat more complex. Milner's intermediate functions $f_n(m)$, $g_n(m)$, and $s(m)$ become modified and less simple.

Lewis has propounded an empirical rule which is equivalent to substituting for C_i (the total equivalent concentration) of the preceding, a quantity S_i called the "ionic strength" and given by

$$S_i = \tfrac{1}{2}\Sigma x_s^2 c_s, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (103)$$

where x_s is the valency of the ion species (s).

It is probably not incompatible with a generalized form of Milner's calculation that this rule should have a certain limited validity as an approximation in practice, but whether it is anything more is rather doubtful.

Chemical reactions in Electrolytic Solutions.

In dilute solutions non-electrolytes behave as perfect solutes for which

$$\frac{\partial\psi}{\partial n_s} = \phi_s - R \log c_s. \quad . \quad . \quad . \quad . \quad . \qquad (104)$$

Not so *ions*, for which, as we have seen,

$$\frac{\partial\psi}{\partial n_s} = \phi_s - R\left\{\log c_s + \Sigma \frac{m_1+1}{2} \phi_1{}' C_i^{m_1}\right\},$$

supposing only ions of the same valency are present.

Now from general theory (equation (21)) in any equilibrium with regard to the virtual chemical change $\Sigma\delta n_s$ we have

$$\Sigma \frac{\partial\psi}{\partial n_s} \,.\, \delta n_s = 0.$$

When all the participants are solutes obeying (104) this gives, as we have seen (and as Planck showed in the case where the solvent is not "associated" or polymerized), the mass-action equation in its ordinary form. When ions participate we get a modified equilibrium-equation.

The case of a weak (or "semi-weak") monobasic acid HA will suffice as an example.

All the δn's are equal, but while

$$\frac{\partial\psi}{\partial n_{\mathrm{HA}}}=\phi_{\mathrm{HA}}-\mathrm{R}\log \mathrm{C}_{\mathrm{HA}},$$

the undissociated molecules behaving as a perfect solute; on the other hand,

$$\left.\begin{aligned}\frac{\partial\psi}{\partial n_{\mathrm{H}'}}&=\phi_{\mathrm{H}'}-\mathrm{R}\log \mathrm{C}_{\mathrm{H}'}-\mathrm{R}\Sigma\frac{m_1+1}{2}\phi_1{}'\mathrm{C}_i^{m_1}\\ \frac{\partial\psi}{\partial n_{\mathrm{A}'}}&=\phi_{\mathrm{A}'}-\mathrm{R}\log \mathrm{C}_{\mathrm{A}'}-\mathrm{R}\Sigma\frac{m_1+1}{2}\phi_1{}'\mathrm{C}_i^{m_1}\end{aligned}\right\}.$$

Whence we get

$$\log\frac{\mathrm{C}_{\mathrm{H}'}\,.\,\mathrm{C}_{\mathrm{A}'}}{\mathrm{C}_{\mathrm{HA}}}=\frac{\phi_{\mathrm{H}'}+\phi_{\mathrm{A}'}-\phi_{\mathrm{HA}}}{\mathrm{R}}-\Sigma(m_1+1)\phi_1{}'\mathrm{C}_i^{m_1} \qquad (105)$$

$$=\log \mathrm{K}-\Sigma(m_1+1)\phi_1{}'\mathrm{C}_i^{m_1}, \quad . \quad . \quad . \qquad (106)$$

which, of course, might have been obtained from the fact that

$$\log\gamma=\tfrac{1}{2}\Sigma(m_1+1)\phi_1{}'\mathrm{C}_i^{m_1},$$

where γ is now the activity coefficient as distinct from the "stoichiometric activity coefficient" generally used by G. N. Lewis.

For the very meaning of γ involves

$$\frac{(\gamma\mathrm{C}_{\mathrm{H}'})(\gamma\mathrm{C}_{\mathrm{A}'})}{\mathrm{C}_{\mathrm{HA}}}=\mathrm{K}.$$

High Concentrations of Electrolytes.

The study of really high concentrations of electrolytes is at present necessarily rather devoid of significance from the point of view of this paper.

Other inter-solute forces enter into the problem, besides the electrostatic forces which no longer remain readily amenable to dynamical calculation, and finally the solvent must necessarily * be a polymerized one of little-known

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* As far as experience goes.

constitution, whereby, as indicated in section IV., very great uncertainties are introduced at high concentrations. It seems advisable, therefore, that the study of strong non-conducting solutions and of non-polymerized solvents should precede that of high concentration conducting solutions.

SUMMARY.

In section I. it is shown that on the basis of a *very* broad assumption, a general treatment of the thermodynamics of any system of phases, from the point of view of molecular theory, can be developed.

This "molecular thermodynamics" which is thus slightly less general than strictly "general thermodynamics" was really initiated by Planck in his classical treatment of a very dilute solution in a non-associated simple solvent.

In section II. the meaning and value of this "molecular" treatment is discussed, and also the general aim and mode of application. It is shown how this treatment paves the way for the introduction of dynamical theory as an aid to the solution of the general problem.

In section III. a slightly modified procedure, useful for many practical cases, is introduced, and the significance of the chief types of experimental data is concisely demonstrated.

Section IV. contains a special treatment of the case of polymerized and mixed solvents, and it is shown how far we can proceed in this case without precise knowledge of the molecular constitution of the solvent.

Some second-approximation equations are put forward for use at medium concentrations, and in an appendix to this section the importance of a second approximation at such concentrations is illustrated by the *non-validity* of the ordinary mass-action equation for perfect solutes.

In section V. the question of electrolytes is considered from the point of view of molecular thermodynamics. It is shown that Milner's calculation of the "virial" of a mixture of ions is of considerable value here, although his application of the Virial theorem is rejected on theoretical grounds. In fact, a striking example of the use of dynamical theory as an aid in the solution of the thermodynamic problem is here forthcoming, and considerable confirmation of the conclusions reached is found in already (recently) established empirical facts.

The question of weak and "semi-strong" electrolytes is

briefly treated as an example of the participation of ions in chemical reactions. Some lines of experimental investigation are indicated in the paper which it is intended to follow up.

In conclusion the author wishes to thank Dr. J W. Nicholson and Mr. H. B. Hartley for encouragement and interest in this paper and for helpful advice with regard to preparation for publication.

Balliol College.
Nov. 10, 1921.

LXXIV. *Notices respecting New Books.*

A Treatise on the Integral Calculus. By JOSEPH EDWARDS, M.A., Principal of Queen's College, London. Vol. I. 907 pages. (Macmillan, 1921; price 50 shillings.)

THIS work when complete will challenge competition with Bertrand's *Calcul intégral*, in size and scope. And the price will make us all reflect, gone up about fivefold by comparison with the pre-war era.

Chapter I leads off in the manner to be anticipated in the modern treatise, with a review of fundamental metaphysical conceptions of difficulties the beginner has not yet encountered, and best kept out of his sight as long as possible.

The author does not settle down in his stride till Chapter II, where it is a comfort to find that the old-fashioned procedure is tolerated of treating Integration as Anti-Differentiation, as leading most rapidly to the applications to give reality to the subject.

Practice is required here as much as in the scale practice of the musician, and this elementary practice is best carried out in the *viva voce* catechetical instruction of a small class, of two or three; in this way the beginner acquires confidence in his initial judgment of the first steps, and can be made to apply them at once to some well chosen elementary applications, and state his result in words. The instructor will be inspired by this treatise in his hand, equivalent of the corresponding German volume by Stegemann.

Real progress has been made in the foreign language when the ear seizes the whole phrase and does not dwell on the separate word. The musician does not read the separate notes of the score, but plays the whole musical phrase, ignoring a misprint.

So too in the Integral Calculus: the object is to see at a glance the nature of the integral, and the class to which it belongs.

A rapid method is described here, p. 179, where the integral is sought as a function of the integrand, as in $\int \sec x\, dx = \mathrm{ch}^{-1} \sec x$, called integration without preparation.

Good instances are provided in Chap. VI, where the integrand is the reciprocal of $a+b\cos x+c\sin x, \ldots$; and the method is developed in Chap. VIII in its application to $\int \frac{\mathrm{M}x+\mathrm{N}}{\mathrm{X}} \frac{dx}{\sqrt{\mathrm{Y}}}$, where X, Y are both quadratics; the substitution $y=\frac{\mathrm{Y}}{\mathrm{X}}$ breaks up the integral without preparation into two simple standard forms, circular and hyperbolic. This integral may be cited as the degenerate hyperelliptic integral, where the sextic under the radical breaks up into $\mathrm{X}^2\mathrm{Y}$. So too when X and Y are both linear, a degenerate elliptic integral is encountered, the cubic under the radical is $\mathrm{X}^2\mathrm{Y}$, having the repeated factor X.

Once started on the Elliptic Integral in Chap. XI, and the author finds it difficult to pull up; we are promised a sequel of complete treatment in vol. II. The lemniscate and cassinian are treated as applications and with elegance, but had better have been delayed till later on. The pious adhesion here to the old standard forms of Legendre should give way to the more elastic treatment of Weierstrass, as not requiring preparation, taking the irrationality in the integrand as reduced to the square root of a cubic; but disregarding the undimensional abstraction of the p function, to consider the Second Stage functions of Abel and Jacobi, where the cubic is resolved into factors

$$\mathrm{X}=4.\ x-x_1 \,.\, x-x_2 \,.\, x-x_3$$

in § 388, and to discuss the various forms that arise and the double periodicity, as the variable x traverses the regions bounded by the branch points x_1, x_2, x_3. As indicated above, with $x_1>x_2>x_3$, the degenerate form is investigated, circular or hyperbolic, as the middle root x_2 moves up to x_1, or down to x_3.

The author works the circular and hyperbolic functions together in harness, and so maintains an analogy of assistance in the treatment. Although so innovating as to introduce the elliptic functions, and to employ the Jacobi-Gudermann notation of sn, cn, dn, and their inverse, he has stopped short of the modern French abbreviations of sh, ch, th, for the hyperbolic functions, analogous to the old sin, cos, tan, of the circular Trigonometry. Bertrand's tangsecthyp strikes us to-day as a very cumbrous form of tanh, or th.

A picture of the integration of $y=x^n$ is provided in fig. 16, p. 112, where the curve PQ then divides the gnomon in the ratio of one to n; this is evident by elementary geometry when Q is brought close up to P, and so still holds as Q separates again to any distance along the curve. Here is the most evident representation of the integration, with no apparent flaw in the argument for the young Berkleian to attack, who is repelled by the gritty approximation he meets in the course of a treatment by summation, necessitating the lengthy abstract apologies of

Chap. I, to meet the objections there suggested, of which the author seems to go in fear.

The integration of the circular functions, $y=\sin x$, $\cos x$, can be shown in a similar picture, equating the differential element of the curve to a corresponding element associated with the circle. No need then for the long-winded summation penultimate to the integral, with its gritty approximation so indigestible to the careful young Berkleian thinker.

The author goes in fear of this young critic, apt to conclude that the Calculus is after all only approximately true; hence much of the lengthy explanations in Chapter I, only to strew his path with difficulty and trip him up.

But if the young heretic will not be convinced in his heresy, agree with him then in his error, and allow that there is an outstanding error, but that the error is finally proved zero. The young engineer is inclined to these heresies, but Perry knew how to interest him.

Perry states the result of a differentiation of $\sin mx$ is to increase the phase angle mx by a lead $\frac{1}{2}\pi$, and to multiply by m;

$$\frac{d}{dx}\substack{\sin\\ \cos}(mx+\epsilon)=m\substack{\sin\\ \cos}(mx+\epsilon+\tfrac{1}{2}\pi),$$

without changing from sine to cosine. Conversely an integration reverses these steps; it subtracts a lag of $\frac{1}{2}\pi$, and divides by m,

$$\int\substack{\sin\\ \cos}(mx+\epsilon)\,dx=\frac{1}{m}\substack{\sin\\ \cos}(mx+\epsilon-\tfrac{1}{2}\pi),$$

and no confused thinking is required of any change of sign.

Similar results are easily remembered for a combination of circular and exponential or hyperbolic functions, expressed in a change of phase and a multiplier or divisor.

The result of the operation of $A\frac{d}{dx}+B$ on $\substack{\sin\\ \cos}(mx+\epsilon)$ is to give a lead $\tan^{-1}\frac{mA}{B}$ and a multiplier $\sqrt{(m^2A^2+B^2)}$; the inverse operation solves the differential equation $A\frac{dy}{dx}+By=\substack{\sin\\ \cos}(mx+\epsilon)$.

The differential equation (D.E.) is not included in the scope of this treatise, and the name even is kept out of sight; so that a third volume looms in the future, to replace the treatise prepared by Bertrand, destroyed in the siege of Paris.

But the novice should become accustomed at the outset to the name and the simple operations. To cure his fright, the integration of $f(x)$ should be proposed as the solution of the D.E. $\frac{dy}{dx}=f(x)$, and then the interpretation of the arbitrary constant, singular solution, node-, tac-, and cusp-locus, can be illustrated in a graph as it occurs.

Take as a type the simple case of the D.E. $\frac{dy}{dx}=\sqrt{x}$.

The solution of the D.E. of the second order with constant coefficients is implied tacitly in all treatises on Physics, in the form $\frac{d^2x}{dt^2}+n^2x=0$ for simple vibration, and the penultimate pendulum oscillation.

We put in a plea here for a return to Aristotle's name of Centre of Gravity, instead of the variants coming in of centroid, centre of mass, of figure, of volume, of inertia.

A mental reservation is implied here of the effect of a radiating field of gravity, on a body according as it is non-centrobaric. This is a refinement that cannot be detected in a careful weighing in a balance, the most accurate operation in a measurement in Physics.

Call the *areal* coordinates of § 460 *centrobaric*, and extend the idea to any number of particles, to make great use of the idea in a number of dynamical problems.

Colonel Hippisley's Ephelkustikon curves deserve mention, as described by a jointed tail, leading sometimes to a good illustration of the asymptotic circle, encountered in some central orbits.

The figures are careful and accurate; and we are spared the too frequent footnote.

There is a copious Table of Contents, but no Index.

LXXV. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from vol. xlii. p. 1024.]

December 7th, 1921.—Mr. H. G. Oldham, F.R.S., President, in the Chair.

THE following communications were read :—

1. 'Jurassic Chronology : II.—Preliminary Studies. Certain Jurassic Strata near Eype's Mouth (Dorset) : the Junction-Bed of Watton Cliff and Associated Rocks.' By S. S. Buckman, F.G.S.

This paper deals with certain Jurassic strata near Eype's Mouth on the coast of Dorset; but, as it forms part of a series of preliminary studies in connexion with Jurassic chronology, certain details connected with other localities are noticed. A general section of the main mass of Watton Cliff east of Eype's Mouth is given. A detailed section is recorded of a remarkable white lithographic bed in Watton Cliff, one in the same position as the Junction-Bed, but differing much in faunal and in stratal details. This bed shows faunal inversion, presumably due to redeposition of material from older deposits.

The dating of this Watton Bed is discussed, after preliminary investigations into the sequence of horizons in the Upper Lias of various areas, in the Junction-Bed, and in the pre-Junction-Bed strata of Thorncombe Beacon. A theory of stratal repetition and coalescence is discussed in regard to the Watton Bed. Its main date is taken to be Yeovilian, *Hammatoceras* hemera. The white lithographic bed of Burton Bradstock is cited as evidence of stratal repetition, and a theory as to the deposition and partial destruction of this Burton bed is put forward.

The Watton and Burton lithographic beds are cited as evidence of Alpenkalk conditions prevailing in Western Europe during two well-separated Jurassic dates, both of them far earlier than the times of Alpenkalk deposits in Central and Eastern Europe.

Certain remarks are made upon sections at Milborne Wick and Haselbury (Somerset) in regard to the dating of their deposits, and a table of the succession and distribution of Hammatoceratids is given.

A palæontological note describes a new species of Rhynchonellid—a species marking a particular deposit at Thorncombe Beacon.

Appendix I, by Mr. James F. Jackson, gives the result of his studies of various sections of the Junction-Bed.

Appendix II, by Dr. L. F. Spath, Mr. J. Pringle, Mr. A. Templeman, and Mr. Buckman, deals with the Upper Liassic sequence, with especial reference to facts disclosed by recent excavations at Barrington (Somerset).

2. 'Banded Precipitates of Vivianite in a Saskatchewan Fireclay.' By John Stansfield, B.A., F.G.S.

A pale-grey Tertiary fire-clay worked for fire-bricks at Clay Bank (Saskatchewan) contains bluish-black spherical, ellipsoidal, and cylindrical patches varying from $\frac{1}{6}$ inch to an inch and a half in greatest dimension. The central portions of the spheres, and the long axes of the cylinders are deeply coloured, and are usually surrounded by a uniformly stained area or by several concentric stained layers of varying, but less intense, tint. The colour is due to an earthy amorphous variety of vivianite, formed presumably by precipitation. The precipitation has been brought about by dilute iron-solutions reacting on solutions of phosphates of organic origin, such solutions being brought together by diffusion through the colloidal matter of the clay. The spacing of the vivianite-bands is irregular, and appears to follow no known law; but similar bands of precipitation may be produced in gelatine by the reaction of certain soluble salts one on the other.

A small specimen of plattnerite (lead dioxide), a very rare mineral recently rediscovered at Leadhills (Lanarkshire), was exhibited by W. Campbell Smith, M.C., M.A,, Sec.G.S.

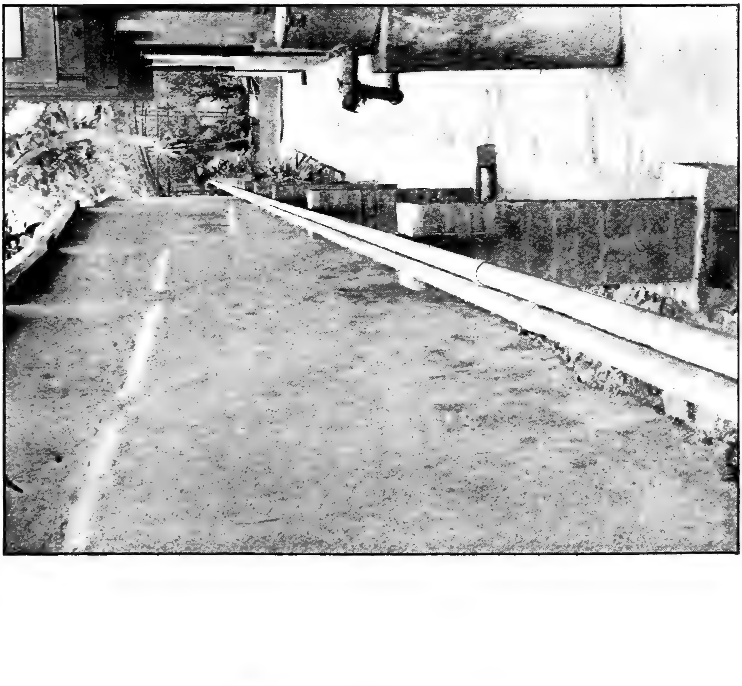


FIG. 2.—Showing 200-foot pipe-line.

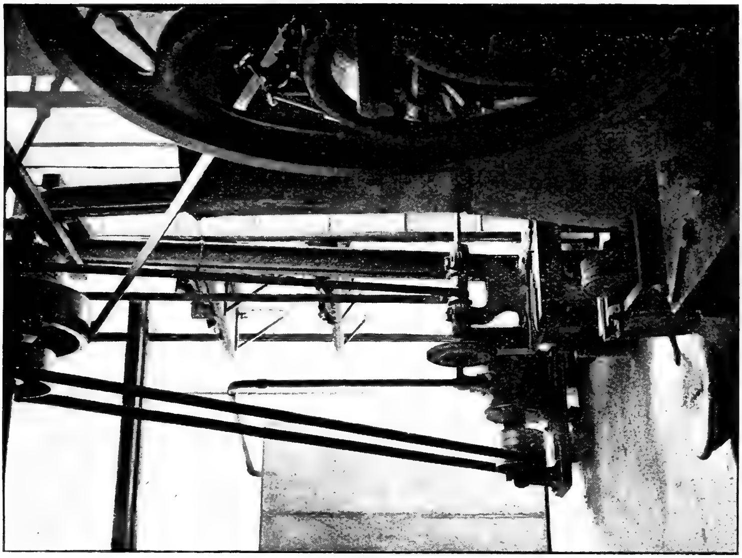


FIG. 3.—Showing Engine, Blower, and Reservoir.

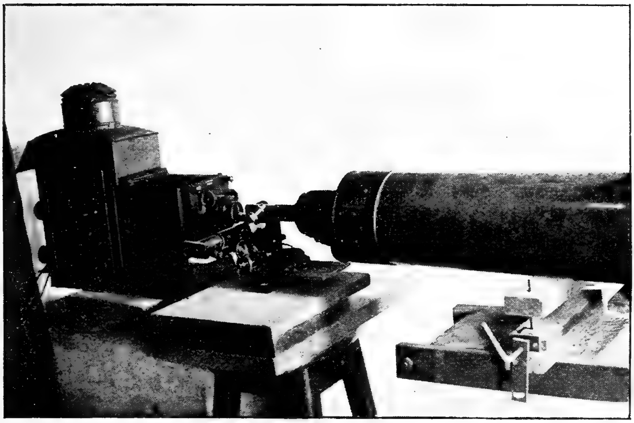


Fig. 4.—Showing observation end.

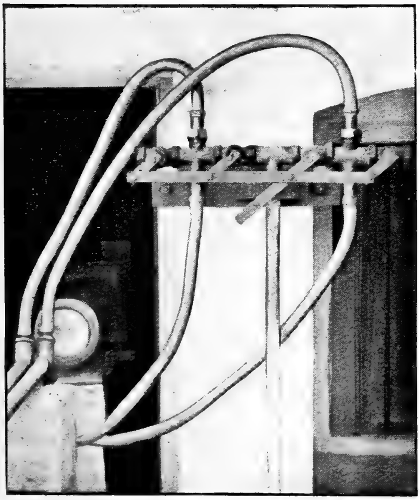
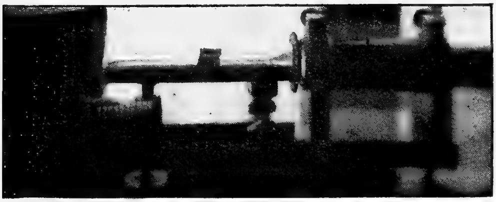


Fig. 5.—Reversing Gear.

Fig. 6.—Showing further end of pipe-line.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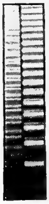
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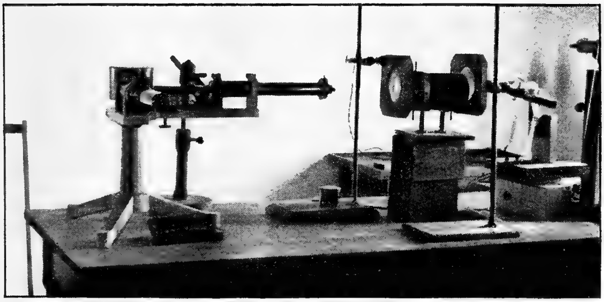
(d)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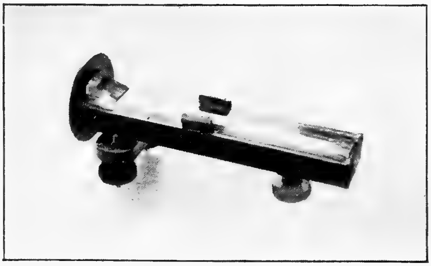
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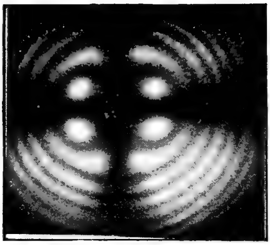
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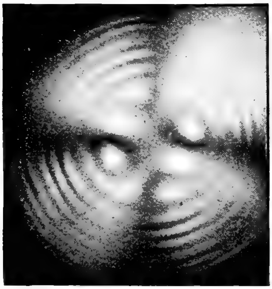
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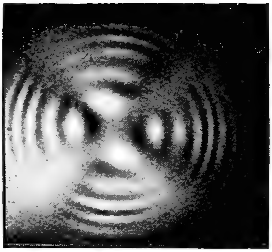
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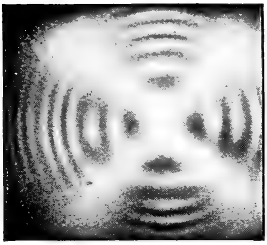
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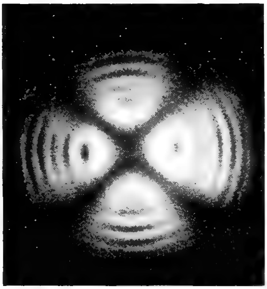
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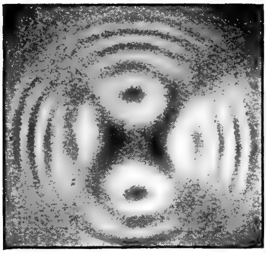
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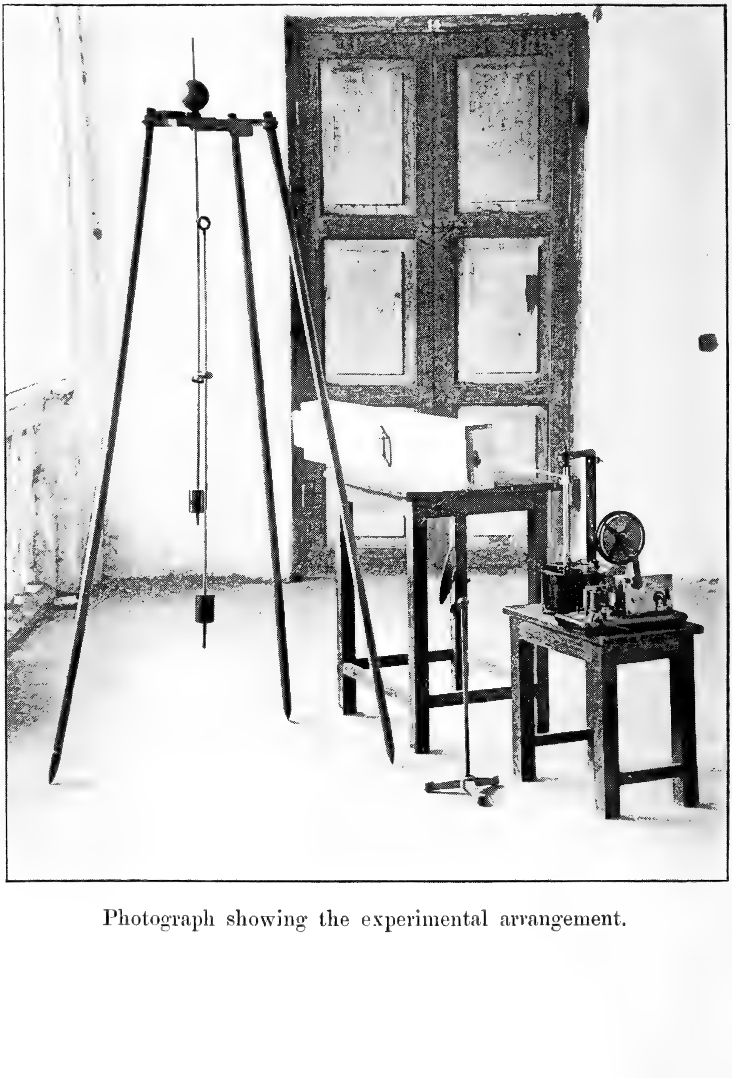
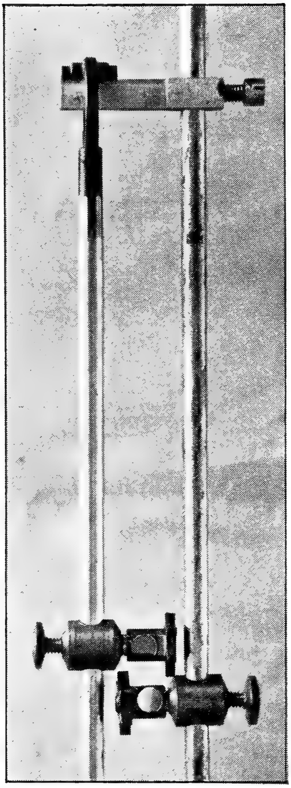


Photograph showing the experimental arrangement.



Photograph showing the optical arrangements.

FIG. 5.

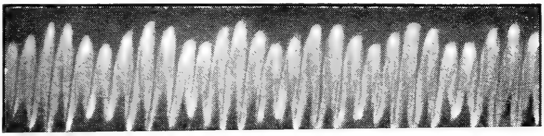
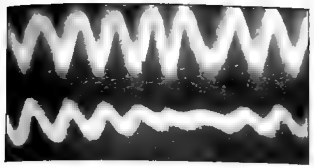
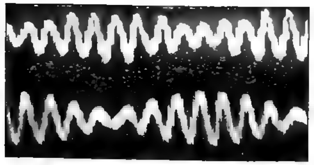


Fig. 1.



5·3

Fig. 2.



10·6

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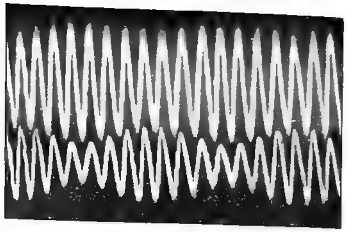
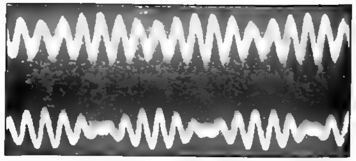


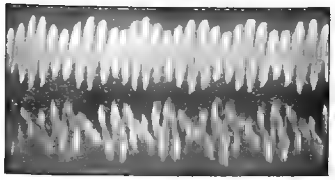
15·7

Fig. 4.



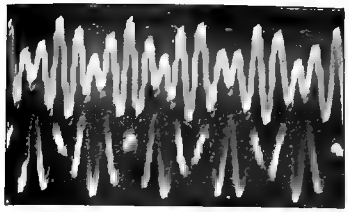
19·8

Fig. 5.



24·7

Fig. 6.



30·5

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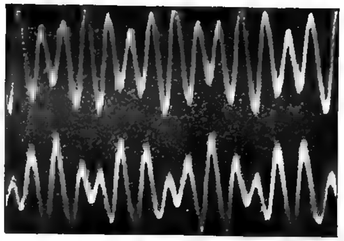
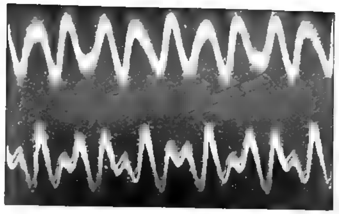


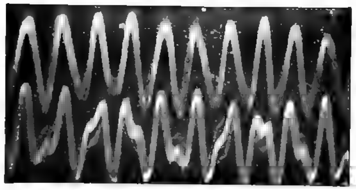
34·6

Fig. 8.



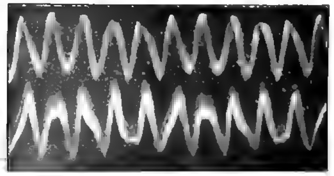
42·6

Fig. 9.



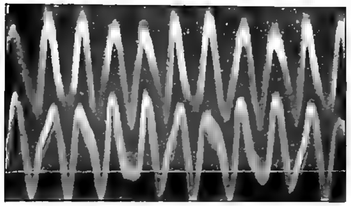
49·5

Fig. 10.



52·8

Fig. 11.



52·8

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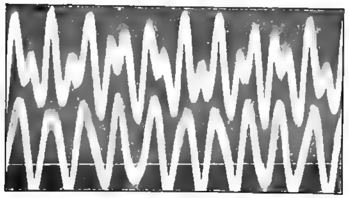

49·5

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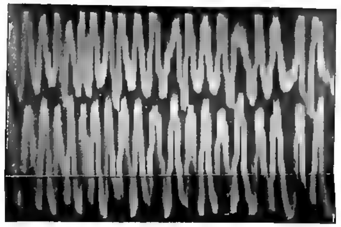
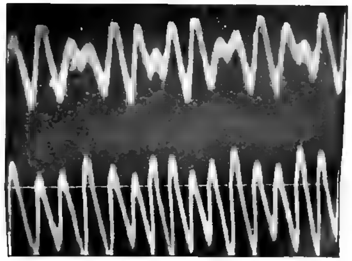


42·6

Fig. 14.



34·6

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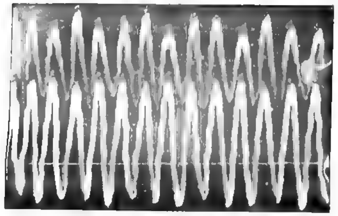

30·5

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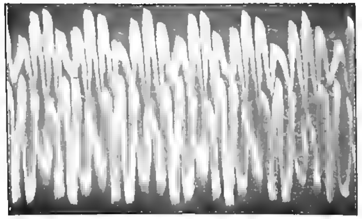

24·7

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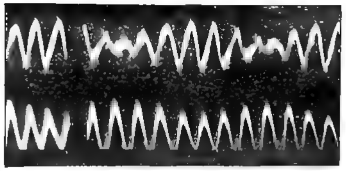

19·8

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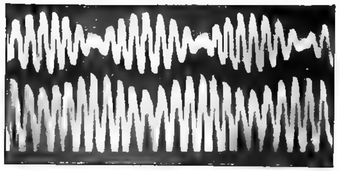

15·7

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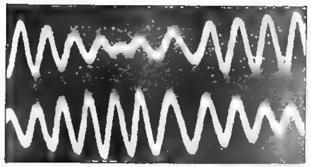

10·6

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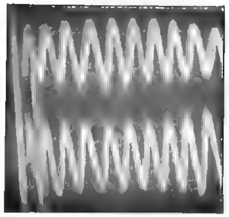


5·3

Fig

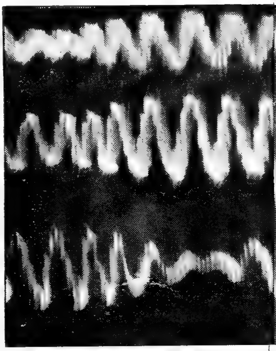


Fig. 2.

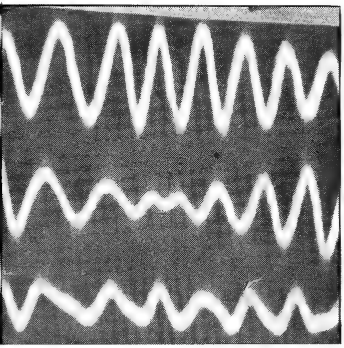
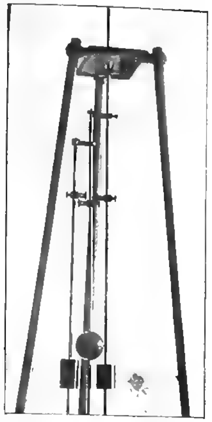


Fig. I.



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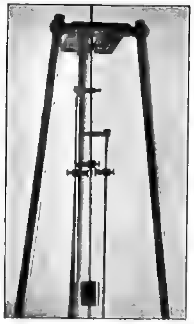
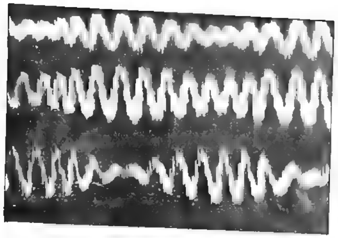


Fig. 1.



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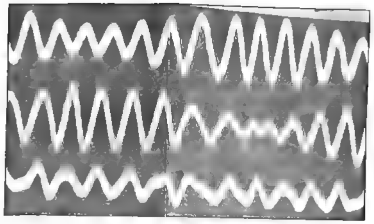

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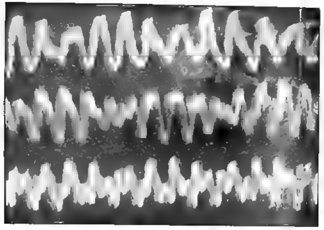

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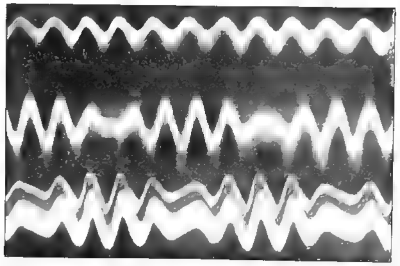

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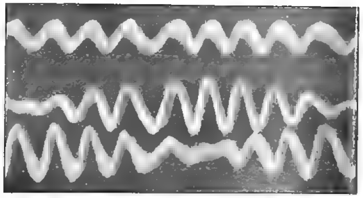

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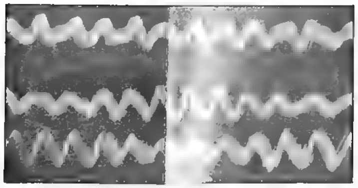

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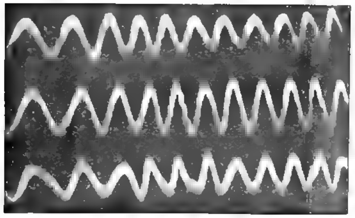

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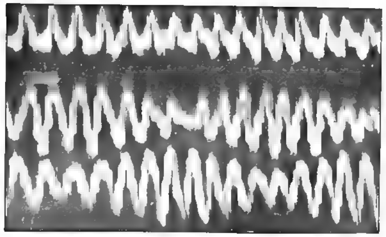

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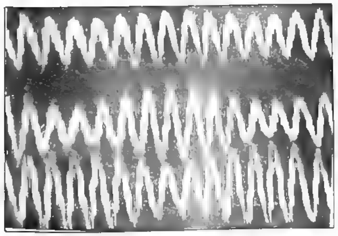

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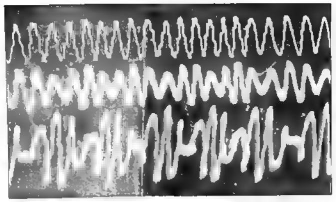

THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SIXTH SERIES.]

APRIL 1922.

LXXVI. *Note on the Theory of Radiation.* *By* C. G. DARWIN, *Fellow and Lecturer of Christ's College, Cambridge* *.

1. THE theory of optics and the thermodynamic theory of radiation both deal with the electromagnetic changes of free space, and yet their methods of treatment are so widely different that hardly any point of contact is to be found in their fundamental definitions and procedure. In optics the primary description is in terms of the electric and magnetic forces, and an arbitrary field is specified by giving those forces at all times and places. On the other hand, in thermodynamics the analysis is entirely different, since it is in terms of radiant energy, passing through every point in every direction and sorted out according to its frequency. Now, though the spectroscope makes it fairly clear what is meant by "the energy in a certain range of frequencies," yet a rigorous definition is lacking, and even the conception of streams of radiation going simultaneously in all directions does not lend itself at once to the ordinary energy formulæ of electromagnetic theory. It appeared to me, therefore, that it might be useful to place on record the formal connexion between the optical and the thermodynamic descriptions of an arbitrary field of radiation; its outline must have been present in the minds of most writers on radiation, but I have not seen it in any work on the subject.

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* Communicated by the Author.

It should be said at once that it seems improbable that any practical use could be made of the relations, or even that an example of them could be given. For in an example it is only possible to specify the optical quantities by virtue of some regularity in their character, and this very regularity makes them unsuited for thermodynamic expression.

2. The only process by which the two types of quantity can be related consists in expressing as integrals the whole flow of energy across an area in terms of both, and then identifying the elements of the two integrands. In no other way can a rigorous definition be given for the thermodynamic quantities. The *modus operandi* consists in the repeated application of Fourier integrals. In the present note no pretence is made to mathematical rigour in the deductions, but there can, I think, be no doubt of their validity. The most important step in the process is based on a theorem, due originally to Stokes [*], and used for the present purpose by Rayleigh [†]. Stokes and Rayleigh both proved this theorem by introducing an exponential factor to help convergence. Here I have not used one, as it would probably be as hard to justify its introduction as to prove rigorously the result without it. To save confusion with a more celebrated theorem, and because Stokes's work dealt with a rather different aspect, I shall call it Rayleigh's theorem. It will be convenient to exhibit it here first, so as to make its repeated use in the later work easier to follow.

Let

$$\left.\begin{aligned}\phi_\nu &= 2\int_{-T/2}^{T/2} Z(t)\cos 2\pi\nu t\,dt,\\ \psi_\nu &= 2\int_{-T/2}^{T/2} Z(t)\sin 2\pi\nu t\,dt,\end{aligned}\right\} \quad . \quad . \quad . \quad (2{\cdot}1)$$

where Z is a function of t, which is restricted in such a way that ϕ_ν and ψ_ν are continuous, and vanish for large values of ν according to some appropriate rule of convergence (the sequel suggests that the necessary condition is $\phi_\nu, \psi_\nu = 0(\nu^{-\frac{1}{2}-\epsilon})$, $\epsilon > 0$), while they vanish for $\nu=0$. T is so large that for $\nu = 0(1/T)$, ϕ_ν and ψ_ν are negligible.

By the principle of the inversion of Fourier integrals, if

$$Z_1 = \int_0^\infty (\phi_\nu \cos 2\pi\nu t + \psi_\nu \sin 2\pi\nu t)\,d\nu, \quad . \quad . \quad (2{\cdot}2)$$

then $Z_1 = Z$ in the interval $\pm T/2$ and vanishes outside it.

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[*] Stokes, Edinb. Trans. xx. p. 317 (1852).

[†] Rayleigh, Phil. Mag. xxvii. p. 460 (1889).

Let $\overline{Z^2}$ be the mean of the square of Z taken over the range $\pm T/2$. Then

$$\overline{Z^2}=\frac{1}{T}\int_{-T/2}^{T/2} Z_1{}^2\,dt$$

$$=\frac{1}{T}\int_{-T/2}^{T/2} dt\int_0^\infty d\nu\int_0^\infty d\nu'(\phi_\nu\cos 2\pi\nu t+\psi_\nu\sin 2\pi\nu t)$$

$$\times(\phi_{\nu'}\cos 2\pi\nu' t+\psi_{\nu'}\sin 2\pi\nu' t).$$

With the restrictions on ϕ_ν and ψ_ν it is permissible to invert the order of integration, and to take that for t first. Then

$$\overline{Z^2}=\frac{1}{2T}\int_0^\infty d\nu\int_0^\infty d\nu'\left\{(\phi_\nu\phi_{\nu'}+\psi_\nu\psi_{\nu'})\frac{\sin\pi(\nu'-\nu)T}{\pi(\nu'-\nu)}\right.$$

$$\left.+(\phi_\nu\phi_{\nu'}-\psi_\nu\psi_{\nu'})\frac{\sin\pi(\nu'+\nu)T}{\pi(\nu'+\nu)}\right\}.$$

Following the usual reasoning for Fourier integrals, with the conditions imposed on T the important part of this is the first term, and for it ν' can be changed into ν in the first factor. Performing the integration for ν', we then have

$$\overline{Z^2}=\frac{1}{2T}\int_0^\infty(\phi_\nu{}^2+\psi_\nu{}^2)d\nu, \quad . \quad . \quad . \quad . \quad (2{\cdot}3)$$

which is the theorem.

There is one point in this result that deserves mention, and that is the presence of the factor 1/T. For at first sight this suggests that if the time considered were long enough, the average would tend to vanish. This is not so, because the magnitudes of ϕ_ν and ψ_ν will vary with T by (2·1). Still if Z were quite arbitrary, $\overline{Z^2}$ would naturally depend on the exact value of T. The utility of (2·3) depends on its application to rather more specialized types of function. For use in radiation theory we must attribute to Z the property which the radiation, in fact, has—that $\overline{Z^2}$ has a value independent of the exact value of T, and ϕ_ν and ψ_ν will then be proportional to $T^{1/2}$. But it does not seem possible to make T disappear from the expression (2·3).

3. The radiation field is specified in the optical manner by means of the six components of electric and magnetic force. To derive from these the thermodynamic description it is necessary first to express the optical quantities as a set of plane waves going in all directions; then the Poynting vector must be calculated from these, and must be integrated

so as to give the total flow of energy through a given aperture in a given time. By successive applications of Rayleigh's theorem the result can be brought to an integral of the same form as the corresponding thermodynamic expression, and the interrelation is then given by equating the two integrands.

Let the optical field be given by X, Y, Z; α, β, γ, which are arbitrary functions of x, y, z, t, subject to their satisfying the electromagnetic equations and to suitable conditions as to continuity and convergence. We shall evaluate the total radiation crossing the yz plane between $y=\pm p/2$ and $z=\pm q/2$ during the time between $t=\pm \mathrm{T}/2$. Here p and q are to be so large that they include many wave-lengths of the types of waves that occur, and the same must be true for T and the periods. On the other hand, they must be sufficiently small to allow for the gross variations of radiation in the different parts of space. These limitations are like those which are imposed in the kinetic theory of gases. More precisely the functions X, Y, Z; α, β, γ are such that the averages to be constructed shall be independent of p, q, and T. It should be said that this independence will not be apparent formally, but will occur in the same way as in (2·3).

4. We proceed to consider how the radiation is to be analysed into plane waves. A typical plane wave is described by the expression

$$\mathrm{S}=g_1^s \cos\tau+g_2^s \sin\tau,$$

where

$$\tau=2\pi\nu\{t-(x\sin\theta\cos\phi+y\sin\theta\sin\phi+z\cos\theta)/c\}, \quad (4·1)$$

while S and g^s represent in turn each of the components of electric and magnetic force according to the rule

$$\left.\begin{array}{ll} g^{\mathrm{X}}=\mathrm{U}\cos\theta\cos\phi-\mathrm{V}\sin\phi & g^{\alpha}=-\mathrm{U}\sin\phi-\mathrm{V}\cos\theta\cos\phi \\ g^{\mathrm{Y}}=\mathrm{U}\cos\theta\sin\phi+\mathrm{V}\cos\phi & g^{\beta}=\mathrm{U}\cos\phi-\mathrm{V}\cos\theta\sin\phi \\ g^{\mathrm{Z}}=-\mathrm{U}\sin\theta & g^{\gamma}=\mathrm{V}\sin\theta \end{array}\right\}. \quad (4·2)$$

Here U corresponds to the wave polarized with electric force in a plane through the z axis and V to that in the perpendicular direction.

The arbitrary field can be represented by taking four quantities U_1, V_1, U_2, V_2 as functions of ν, θ, ϕ and expressing any of the forces as

$$\mathrm{S}=\int_0^\infty d\nu\int_0^\pi \sin\theta\, d\theta\int_0^{2\pi} d\phi(g_1^s\cos\tau+g_2^s\sin\tau).$$

As we are to consider the flow of energy through the aperture in the yz plane, we put $x=0$ in this expression, thus changing τ into

$$\tau_0=2\pi\nu\{t-(y\sin\theta\sin\phi+z\cos\theta)/c\}.$$

But now a difficulty arises in determining the g's, for no one of the forces by itself can determine whether the wave is going forwards or backwards. This difficulty is reflected in the mathematics, for in the ϕ integration τ_0 assumes all its values twice over, which prevents the usual inversion. To obviate this, we separate out and add together the g's corresponding to ϕ and $\pi-\phi$ and take the ϕ integration between $\pm\pi/2$. Thus, if

$$G^s=g^s(\nu,\theta,\phi)+g^s(\nu,\theta,\pi-\phi),$$

we take as the typical formula

$$S_1=\int_0^\infty d\nu\int_0^\pi\sin\theta\,d\theta\int_{-\pi/2}^{\pi/2}d\phi(G_1{}^s\cos\tau_0+G_2{}^s\sin\tau_0). \quad (4\cdot3)$$

These considerations show what formulæ are aimed at. To obtain them put

$$G_1{}^s=2\frac{\nu^2}{c^2}\sin\theta\cos\phi\int_{-p/2}^{p/2}dy\int_{-q/2}^{q/2}dz\int_{-T/2}^{T/2}dt\,S(0,y,z,t)\cos\tau_0 \quad . \quad (4\cdot4)$$

and a similar expression in $G_2{}^s$ and $\sin\tau_0$. Then, by three successive inversions for ϕ, θ, and ν in turn, it may be shown that $S_1=S$ between the limits $\pm p/2$, $\pm q/2$, $\pm T/2$ and vanishes outside them. Knowing the G_1's we are thus led to six equations of the type of (4·2), of which the first is, for instance,

$$\begin{aligned}G_1{}^X=[U_1(\phi)-U_1(\pi-\phi)]\cos\theta\cos\phi\\ -[V_1(\phi)+V_2(\pi-\phi)]\sin\phi. \quad . \quad (4\cdot5)\end{aligned}$$

and there are six similar equations in G_2, U_2, V_2. The U's and V's can be determined from these, and give

$$\left.\begin{aligned}U(\phi)&=\{-G^Z\cos\phi+G^\beta\sin\theta+G^\gamma\cos\theta\sin\phi\}/2\sin\theta\cos\phi\\ V(\phi)&=\{\quad G^\gamma\cos\phi+G^Y\sin\theta+G^Z\cos\theta\sin\phi\}/2\sin\theta\cos\phi\end{aligned}\right\}. \quad (4\cdot6)$$

There are similar equations for $U(\pi-\phi)$ and $V(\pi-\phi)$ and two redundant equations of the form

$$\left.\begin{aligned}G^X&=G^\beta\cos\theta-G^\gamma\sin\theta\sin\phi\\ -G^\alpha&=G^Y\cos\theta-G^Z\sin\theta\sin\phi\end{aligned}\right\}, \quad . \quad . \quad (4\cdot7)$$

which must be satisfied identically. That they are, may be seen from the fact that, expressed in terms of the forces X etc. by (4·4), they are simply those two of the electromagnetic equations which do not involve the operator $\partial/\partial x$—that is, which are valid on the yz plane.

5. We next find the flow of energy through the aperture, and apply Rayleigh's theorem to it. The flow in the positive direction of x per unit area per unit time is the component of the Poynting vector $(\mathrm{Y}\gamma-\mathrm{Z}\beta)c/4\pi$, and so the total flow through the aperture in time T is F, where

$$\left.\begin{aligned}\mathrm{F}&=\frac{c}{4\pi}\int_{-p/2}^{p/2}dy\int_{-q/2}^{q/2}dz\int_{-\mathrm{T}/2}^{\mathrm{T}/2}dt(\mathrm{Y}_1\gamma_1-\mathrm{Z}_1\beta_1)\\&=\frac{c}{4\pi}\int_{-p/2}^{p/2}dy\int_{-q/2}^{q/2}dz\int_{-\mathrm{T}/2}^{\mathrm{T}/2}dt\int_0^{\infty}d\nu\int_0^{\pi}\sin\theta\,d\theta\int_{-\pi/2}^{\pi/2}d\phi\\&\qquad\qquad\int_0^{\infty}d\nu'\int_0^{\pi}\sin\theta'\,d\theta'\int_{-\pi/2}^{\pi/2}d\phi'\\&\quad\Big[\{\mathrm{G}_1{}^{\mathrm{Y}}\cos\tau_0+\mathrm{G}_2{}^{\mathrm{Y}}\sin\tau_0\}\{\mathrm{G}_1{}^{\gamma'}\cos\tau_0'+\mathrm{G}_2{}^{\gamma'}\sin\tau_0'\}\\&\quad-\{\mathrm{G}_1{}^{\mathrm{Z}}\cos\tau_0+\mathrm{G}_2{}^{\mathrm{Z}}\sin\tau_0\}\{\mathrm{G}_1{}^{\beta'}\cos\tau_0'+\mathrm{G}_2{}^{\beta'}\sin\tau_0'\}\Big]\end{aligned}\right\}\quad .\quad(5{\cdot}1)$$

In this $\mathrm{G}_1{}^{\beta'}$ is the same function as $\mathrm{G}_1{}^{\beta}$, but with arguments ν', θ', ϕ', and τ_0' is the same as τ_0, but with arguments $\nu', \theta', \phi', y, z, t$.

To avoid writing out many terms which will afterwards vanish in the integrations, observe that in this expression only those arising out of $\frac{1}{2}\cos(\tau_0-\tau_0')$ will contribute anything, and that those consist of the sum of identical terms in G_1's and G_2's. We shall therefore only consider the former. Reverse the order of the integrations and perform those for y, z, t; then

$$\begin{aligned}\mathrm{F}=\frac{c}{4\pi}\frac{1}{2}\int^{(6)}&d\nu\,d\theta\,d\phi\,d\nu'\,d\theta'\,d\phi'\sin\theta\sin\theta'\{\mathrm{G}_1{}^{\mathrm{Y}}\mathrm{G}_1{}^{\gamma'}-\mathrm{G}_1{}^{\mathrm{Z}}\mathrm{G}_1{}^{\beta'}\}\\&\frac{\sin\pi(\nu'-\nu)\mathrm{T}}{\pi(\nu'-\nu)}\,\frac{\sin\pi(\nu'\sin\theta'\sin\phi'-\nu\sin\theta\sin\phi)p/c}{\pi(\nu'\sin\theta'\sin\phi'-\nu\sin\theta\sin\phi)/c}\\&\qquad\frac{\sin\pi(\nu'\cos\theta'-\nu\cos\theta)q/c}{\pi(\nu'\cos\theta'-\nu\cos\theta)/c}\quad .\quad .\quad(5{\cdot}2)\end{aligned}$$

Now integrate for ν'. This removes the first factor of the second line and changes ν' into ν in the rest. Next, the θ' integration removes the factor in the third line, giving a multiplier $c/\nu\sin\theta$ and changing θ' into θ in the rest. Then the ϕ' integration removes the middle factor, giving a multiplier $c/\nu \sin\theta\cos\phi$ and changing ϕ' into ϕ. Thus

$$F=\frac{c}{8\pi}\int_0^\infty d\nu\int_0^\pi d\theta\int_{-\pi/2}^{\pi/2} d\phi\{G_1{}^{Y}G_1{}^{\gamma}-G_1{}^{Z}G_1{}^{\beta}\}c^2/\nu^2\cos\phi. \quad (5{\cdot}3)$$

Now substitute for the G_1's in terms of U_1 and V_1. By (4·2) and (4·5)

$$G_1{}^{Y}G_1{}^{\gamma}-G_1{}^{Z}G_1{}^{\beta}=\sin\theta\cos\phi[U_1{}^2(\phi)+V_1{}^2(\phi)$$
$$-U_1{}^2(\pi-\phi)-V_1{}^2(\pi-\phi)].$$

So if we denote $U_1{}^2+U_2{}^2$ by U^2, we have finally

$$F=\frac{c^3}{8\pi}\int_0^\infty\frac{d\nu}{\nu^2}\int_0^\pi\sin\theta\, d\theta\int_{-\pi/2}^{\pi/2} d\phi[U^2(\phi)+V^2(\phi)$$
$$-U^2(\pi-\phi)-V^2(\pi-\phi)]. \quad (5{\cdot}5)$$

6. For the thermodynamic treatment of radiation * we take an aperture $d\sigma$, and from it, at angle ϵ to the normal, draw a cone of small solid angle $d\omega$. The energy passing through the aperture into this cone in time dt is supposed separated into its two components of polarization and analysed into its frequencies, so that the specification of the field is

$$(K_\nu+K_\nu{}')\,d\nu\, d\sigma\cos\epsilon\, d\omega\, dt. \quad . \quad . \quad . \quad (6{\cdot}1)$$

Here we are to take

$$d\sigma=pq,\quad \cos\epsilon=\sin\theta\cos\phi,\quad d\omega=\sin\theta\, d\theta\, d\phi,\quad dt=T.$$

Let K_ν refer to the component polarized with electric force in a plane through the z axis. Then the whole excess of energy going in the positive direction is

$$F=pqT\int_0^\infty d\nu\int_0^\pi\sin\theta\, d\theta\int_{-\pi/2}^{\pi/2} d\phi[K_\nu(\phi)+K_\nu{}'(\phi)$$
$$-K_\nu(\pi-\phi)-K_\nu{}'(\pi-\phi)]\sin\theta\cos\phi. \quad (6{\cdot}2)$$

If we equate the terms of this integrand to those of (5·5), we have

$$\left.\begin{aligned}K_\nu &=c^3U^2/8\pi\nu^2\,.\sin\theta\cos\phi\,.\,pqT\\ K_\nu{}' &=c^3V^2/8\pi\nu^2\,.\sin\theta\cos\phi\,.\,pqT\end{aligned}\right\}, \quad . \quad . \quad (6{\cdot}3)$$

and these constitute the formal definitions of K_ν and $K_\nu{}'$.

Just as in § 2 we saw that $\overline{Z^2}$ involved T explicitly, though

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* See Planck, *Vorlesungen über die Theorie der Wärmestrahlung* (Barth). Many of the relations, which he proves with some difficulty by Fourier series, come out much easier with Fourier integrals.

really it would be independent, so here K_ν appears to involve p, q, T. It also involves the factor $\sin\theta\cos\phi$ and at first sight it seems that this should have disappeared in the course of the calculations, since it arises from the $\cos\epsilon$ in (6·1) and simply means that the cone of rays may be cut by a plane in any direction to give the aperture. But, in effect, this corresponds to taking a new aperture—that is, new values for p and q,—and as it is not possible to verify that such a change is immaterial even when the plane of the aperture is unchanged, *a fortiori*, it will not be possible when the plane is changed as well. We can only say that if a real radiation field were specified in the optical manner, and if the calculations of §§ 4, 5, and 6 were applied to it, we should find that the resulting K_ν was independent of the time and of both the area and direction of the aperture.

If the values of U and V are written in from (4·6) and (4·4), we have in full

$$K_\nu = \frac{1}{pqT\sin\theta\cos\phi}\frac{\nu^2}{8\pi c}\int_{-p/2}^{p/2}dy\int_{-q/2}^{q/2}dz\int_{-T/2}^{T/2}dt\int_{-p/2}^{p/2}dy'\int_{-q/2}^{q/2}dz'$$

$$\int_{-T/2}^{T/2}dt'\cos 2\pi\nu\{(t-t')-[(y-y')\sin\theta\sin\phi+(z-z')\cos\theta]/c\}$$

$$\times(-Z\cos\phi+\beta\sin\theta+\gamma\cos\theta\sin\phi)$$

$$\times(-Z'\cos\phi+\beta'\sin\theta+\gamma'\cos\theta\sin\phi),\quad . \quad (6\cdot4)$$

where Z′, etc. are the same as Z, etc., taken with arguments y', z', t'. For K_ν' the brackets are

$$(\gamma\cos\phi+Y\sin\theta+Z\cos\theta\sin\phi),\text{ etc.}$$

and otherwise the expression is the same. The relation (6·4) can be put into other forms by virtue of (4·7). A particularly simple case is that of the radiation going normally from the aperture, which is found by putting $\theta=\pi/2$, $\phi=0$. $K_\nu^{x,z}$ signifies the K_ν of the ray going along the x axis and polarized with electric force in the xz plane.

$$K_\nu^{x,z} = \frac{1}{pqT}\frac{\nu^2}{8\pi c}\int_{-p/2}^{p/2}dy\int_{-q/2}^{q/2}dz\int_{-T/2}^{T/2}dt\int_{-p/2}^{p/2}dy'\int_{-q/2}^{q/2}dz'$$

$$\int_{-T/2}^{T/2}dt'\cos 2\pi\nu(t-t')(\beta-Z)(\beta'-Z'). \quad (6\cdot5)$$

For $K_\nu^{x,y}$ the last two factors must be replaced by $(\gamma+Y)$ $(\gamma'+Y')$.

This completes the problem of formally expressing the thermodynamic specification of the field in terms of the optical.

LXXVII. *Thermodynamical Theory of Surface Tension. By* SHIZUWO SANO, *Physical Institute, Imperial University of Tokyo* *.

IN this paper I am going to present to the reader a thermodynamical theory of surface tension in the transition layer between fluids, based on several assumptions, some of which are quite arbitrary.

Let us consider two fluids in contact and in equilibrium, and the layer of transition between the fluids not charged with electricity, except for the fact that the layer is a double sheet.

In this paper it is assumed that (i.) some of the chemical constituents of which the two fluids in contact with each other are made are electrolytic ions unless the contrary is stated, and at every point each of the densities $\rho_1, \rho_2, \ldots \rho_n$ is not absolutely zero, where ρ_i is the density of the i-th constituent; (ii.) the free energy per unit volume F is a function of the absolute temperature θ and the n densities $\rho_1, \rho_2, \ldots \rho_n$, but is independent of the space variations of these quantities; (iii.) F depends not only on σ, but on $\frac{\partial\sigma}{\partial x}, \frac{\partial\sigma}{\partial y}, \frac{\partial\sigma}{\partial z}$, and not on the higher space variations of σ, where σ is a scalar quantity defining the state of aggregation; (iv.) F is a continuous function of the $n+8$ independent variables $\sigma, \sigma_x, \sigma_y, \sigma_z, \theta, \rho_1, \rho_2 \ldots \rho_n$, D_x, D_y, D_z, where $\sigma_x, \sigma_y, \sigma_z$ stand for $\frac{\partial\sigma}{\partial x}, \frac{\partial\sigma}{\partial y}, \frac{\partial\sigma}{\partial z}$ respectively, and D_x, D_y, D_z are the components of the electric displacement; (v.) all the independent variables $\sigma, \sigma_x, \sigma_y, \sigma_z, \theta, \rho_1, \rho_2, \ldots \rho_n, D_x$, D_y, D_z are continuous functions of the rectangular co-ordinates x, y, z; (vi.) F is sensibly independent of $\sigma_x, \sigma_y, \sigma_z$ in all the points outside of the transition layer; and (vii.) the elementary work done per unit volume on the electric field when the densities are kept constant is

$$E_x dD_x + E_y dD_y + E_z dD_z,$$

where E_x, E_y, E_z are the components of the electric force.

The quantity σ above stated requires some explanation. The functional form of F differs according as we take the first fluid or the second. For the first fluid we put $\sigma = \sigma'$, a

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* Communicated by Prof. A. W. Porter, F.R.S.

constant, for every point in the fluid for all values of θ, ρ_1, ρ_2, . . . ρ_n, D_x, D_y, D_z. For every point of the second fluid, is assigned another constant value of σ, say σ''. I consider every point in the transition layer on a line normal to the layer to have different values of σ varying from σ' to σ''.

It was hinted in my former paper on the equilibrium of fluids in an electromagnetic field * that a theory explaining the existence of surface tension can be formed by assuming that F contains σ_x, σ_y, σ_z. According to my theory, every point along the orthogonal line in the transition layer is in a different state of aggregation and is in stable equilibrium, both mechanically and chemically, although I shall not enter into any investigation of the conditions of stability. Though I assume that the fluids vary continuously from one phase to the other, the conception differs entirely from that contained in van der Waals's equation of condition.

In the paper referred to, I proved that the conditions of chemical equilibrium are

$$\frac{\partial F}{\partial \rho_i} + q_i\Psi_e + \Psi_g = C_i, \; [i=1, 2, 3, \ldots n], \quad . \quad . \quad (1)$$

where Ψ_e and Ψ_g are electric and gravitational potentials respectively, and q_i the quantity of electricity associated with the unit mass of the i-th constituent, and C_i is independent of x, y, z. In obtaining (1) it was assumed that the gravitational field was uniform, but it can be easily seen that the proof is more general. In (1) the effect of mutual gravitational attraction of different portions of the fluids under consideration is neglected.

It was also proved that if there is a reaction equation of the form

$$\Sigma \nu_i S_i = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where S_i represents a molecule of the i-th constituent and ν's are integers, then the equation of chemical equilibrium corresponding to the reaction (2) is

$$\Sigma \nu_i m_i \frac{\partial F}{\partial \rho_i} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

m_i being the molecular weight of the i-th constituent.

Proceeding in a similar way as in my paper above mentioned, the equations of mechanical equilibrium are easily

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* Proc. Math.-Phys. Soc. Tokyo, ii. p. 365 (1905); *Physik. Zeitschr.* vi. p. 566 (1905).

found to be

$$\left.\begin{aligned}
\mathrm{X}=&\frac{\partial}{\partial x}\left\{-\mathrm{F}+\sigma_x\frac{\partial \mathrm{F}}{\partial\sigma_x}+\sum_{i=1}^{i=n}\rho_i\frac{\partial \mathrm{F}}{\partial\rho_i}+\mathrm{E}_y\mathrm{D}_y+\mathrm{E}_z\mathrm{D}_z\right\}\\
&+\tfrac{1}{2}\frac{\partial}{\partial y}\left\{\sigma_x\frac{\partial \mathrm{F}}{\partial\sigma_y}+\sigma_y\frac{\partial \mathrm{F}}{\partial\sigma_x}-\mathrm{E}_x\mathrm{D}_y-\mathrm{E}_y\mathrm{D}_x\right\}\\
&+\tfrac{1}{2}\frac{\partial}{\partial z}\left\{\sigma_z\frac{\partial \mathrm{F}}{\partial\sigma_x}+\sigma_x\frac{\partial \mathrm{F}}{\partial\sigma_z}-\mathrm{E}_z\mathrm{D}_x-\mathrm{E}_x\mathrm{D}_z\right\},\\
\mathrm{Y}=&\ \ldots,\\
\mathrm{Z}=&\ \ldots,
\end{aligned}\right\}. \qquad (4)$$

where X, Y, Z are the components of the impressed force per unit volume.

Now, suppose that the layer of transition is not placed under an external electric field, so that we may take the component electric force parallel to the surface $\sigma=$const., which passes through the point under consideration, to vanish.

When the capillary layer is not horizontal, there will be a component of the electric force parallel to the layer, due to the effect of gravity, but this is so small that for all practical purposes it may be neglected. The electric displacement outside the layer is, by the same reasoning, taken to be zero.

Let us consider a line orthogonal to the series of surfaces $\sigma=$ const. and take two points P′ and P″ on this line, P′ being in the first fluid and P″ in the second, both being very near to the transition layer ; and let ds be the element of the line. Then it immediately follows from (4) that the surface tension is

$$\mathrm{T}=\int\left(\sigma_s\frac{\partial \mathrm{F}}{\partial\sigma_s}-\mathrm{ED}\right)ds, \quad . \quad . \quad . \quad (5)$$

where σ_s denotes the magnitude of the vector $(\sigma_x, \sigma_y, \sigma_z)$, and E and D are the electric force and electric displacement respectively, and the integral is to be taken from P′ to P″. By dint of these suppositions, the position of P′ along the curve does not alter the value of the right-hand side of (5) so long as P′ lies outside the transition layer.

Now suppose that the axis of x is vertical, and that the surfaces $\sigma=$const. are horizontal planes and that the variables are independent of y and z. In this case we may write (5) in the form

$$\mathrm{T}=\int\left(\sigma_x\frac{\partial \mathrm{F}}{\partial\sigma_x}-\mathrm{ED}\right)dx. \quad . \quad . \quad . \quad . \quad (6)$$

If ρ_e denotes the electric charge per unit volume, then

$$\rho_e = \sum_{i=1}^{i=n} q_i \rho_i = \frac{\partial \mathrm{D}}{\partial x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

so that (6) may be written

$$\mathrm{T} = \int \left(\sigma_x \frac{\partial \mathrm{F}}{\partial \sigma_x} - \Psi_e \rho_e \right) dx, \quad . \quad . \quad . \quad . \quad (8)$$

since D vanishes at P′ and P″.

The phenomena of pyro-electricity teach us that E does not vanish at the same time as D in crystals having polar axes. It seems to me that it is quite natural to suppose that at any point P within the transition layer the fluid may be considered just like a crystal having a polar axis, normal to the series of surfaces $\sigma=$const., *i. e.* the electric force $\frac{\partial \mathrm{F}}{\partial \mathrm{D}}$ contains σ_x and does not vanish when $\mathrm{D}=0$. If this is really the case, both $\sigma_x \frac{\partial \mathrm{F}}{\partial \sigma_x}$ and $\Psi_e \rho_e$ contain terms depending upon the distribution of electricity in the layer of transition, so that it is impossible to conceive that $-\int \psi_e \rho_e \, dx$ would be the term arising from the double sheet of electricity in the layer.

If we assume that F is independent of σ_x, then (6) would become

$$\mathrm{T} = -\int \mathrm{ED} \, dx,$$

where E vanishes simultaneously with D. Since we expect that E and D have the same sign at P, this value of T would become negative, *i. e.* the mechanical equilibrium would be labile. Hence if we assume that F is independent of σ_x, then the fluid cannot exist in two phases in contact. Discussing this from another point of view :—

In the following, I assume that the temperature is given, and neglect the effect of gravity altogether. Let the quantities referring to the point P′ be accented once, and those corresponding to P″ twice.

Now, assuming that F does not contain σ_x, then from (1), (3), (4) we get

$$\frac{\partial \mathrm{F}'}{\partial \rho_i'} + q_i (\Psi_e' - \Psi_e'') = \frac{\partial \mathrm{F}''}{\partial \rho_i''}, \ [i=1, 2, \ldots n], \quad . \quad (9)$$

$$\Sigma \nu_i m_i \frac{\partial \mathrm{F}'}{\partial \rho_i'} = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$-\mathrm{F}' + \Sigma \rho_i' \frac{\partial \mathrm{F}'}{\partial \rho_i'} = -\mathrm{F}'' + \Sigma \rho_i'' \frac{\partial \mathrm{F}}{\partial \rho_i''}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

First, suppose that there is only one independent constituent, and that all the molecules are electrically neutral. Let there be $n-1$ kinds of molecules $S_2, S_3, \ldots S_n$, all of which are formed by the polymerization of S_1. In this case there are $n-1$ equations of the type (10), so that there are $2n$ equations (9), (10), and (11) determining $2n$ unknown quantities $\rho_1', \rho_2', \ldots \rho_n', \rho_1'', \rho_2'', \ldots \rho_n''$. Hence the constants C in the equations

$$\frac{\partial F}{\partial \rho_i} = \frac{\partial F'}{\partial \rho_i'} = C_i, \ [i=1, 2, \ldots n], \quad . \quad . \quad (12)$$

$$-F + \Sigma \rho_i \frac{\partial F}{\partial \rho_i} = C_{n+1} \ . \quad . \quad . \quad . \quad . \quad (13)$$

become determinate. Since we have supposed that all the molecules are electrically neutral, $\frac{\partial D}{\partial x} = 0$, from which we have $D=0$, since by our supposition D vanishes at P' and P''. Hence F contains only n unknown quantities $\rho_1, \rho_2, \ldots \rho_n$ for any value of σ between σ' and σ''. But these quantities would have to satisfy $n+1$ equations (12) and (13), which is impossible.

Next, take the case of the system composed of h independent constituents, the molecules of which are all supposed to be electrically neutral. In this case there are $n-h$ independent reaction equations of the form (2), to which correspond $n-h$ equations of the type (10). Since we can give any assigned values to $\rho_2'/\rho_1', \rho_3'/\rho_1', \ldots \rho_h'/\rho_1'$ between proper limits, $2n$ unknown quantities $\rho_1', \rho_2', \ldots \rho_n', \rho_1'', \rho_2'', \ldots \rho_n''$ are determinate corresponding to any set of values of $\rho_2'/\rho_1', \ldots \rho_h'/\rho_1'$, so that $C_1, C_2, \ldots C_{n+1}$ become determinate. Just as in the preceding case in which there is only one independent constituent, the n densities $\rho_1, \rho_2, \ldots \rho_n$ would have to satisfy $n+1$ equations (12) and (13) in the interior of the transition layer.

Thus, if we suppose that there are only neutral molecules in the fluids, and also assume that F is independent of σ_x, then it follows that it is impossible to consider that there would be a transition layer in equilibrium between two fluids.

Next, suppose that F is again independent of σ_x, and that there are electrolytically dissociated molecules.

First, take the case in which the two fluids consist of only one independent constituent, so called. In this case the molecules $S_1, S_2, \ldots S_n$ are connected by $n-2$ independent reaction equations, and the $2n+1$ unknown quantities $\rho_1', \rho_2', \dots \rho_n', \rho_1'', \rho_2'', \dots \rho_n'', \Psi_e''-\Psi_e'$ are determined by $2n+1$ unknown quantities $\rho_1', \rho_2', \dots \rho_n', \rho_1'', \rho_2'', \dots \rho_n''$, $\Psi''-\Psi_e'$ are determined by $2n+1$ equations (9), (10), (11), and

$$\Sigma q_i \rho_i'=0, \quad \Sigma q_i \rho_i''=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Hence, if we write

$$\frac{\partial \mathrm{F}}{\partial \rho_i}+q_i(\Psi_e-\Psi_e')=\mathrm{G}_i, \ [i=1, 2, \dots n], \ . \quad (15)$$

$$-\mathrm{F}+\Sigma\rho_i\frac{\partial \mathrm{F}}{\partial \rho_i}=\mathrm{G}_{n+1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

then the constants G are determined quantities. Solving the $n+1$ equations (15) and (16), the $n+1$ quantities $-(\Psi_e-\Psi_e')$, $\rho_1, \rho_2, \dots \rho_n$ and also the right-hand side of the equation

$$\frac{\partial \mathrm{D}}{\partial x}=\Sigma q_i \rho_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

become functions of D and σ only. Differentiating $\Psi_e'-\Psi_e$ with respect to x and making use of the equation

$$\mathrm{E}=\frac{\partial \mathrm{F}}{\partial \mathrm{D}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and then eliminating D, we get an equation in the form

$$f_1\left(\sigma, \frac{d\sigma}{dx}, \frac{d^2\sigma}{dx^2}\right)=0,$$

from which we deduce a solution of the form

$$\sigma=f_2(x+\mathrm{A}, \mathrm{B}), \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where A and B are constants of integration.

During the process of reaching the final solution of σ as a function of x, we have differentiated $\Psi_e'-\Psi_e$ with respect to x, so that we cannot expect (19) to satisfy the condition that $\Psi_e'-\Psi_e$ vanishes at P′, unless the arbitary constants in (19) are so chosen as to satisfy the condition. All the solutions of (17) satisfy the condition $\frac{\partial \mathrm{D}}{\partial x}=0$ at $\sigma=\sigma'$, but not $\mathrm{D}=0$ at the same point. Hence, in order that equation (19) may be our solution, it must satisfy the three conditions that $\Psi_e-\Psi_e'$ and D vanish at P′ and σ becomes σ' at the same point. But (19) contains only two arbitrary constants, so that it cannot satisfy all these three conditions. Therefore in this case the transition layer cannot exist.

It will be remarked that in this case the transition layer is just like a fluid in which there are two independent constituents, since n kinds of molecules are connected with each other by only $n-2$ independent reaction equations.

In the case in which there are more independent constituents, the reasoning quite similar to the above holds good, and we see that the neglecting of terms containing σ_x in the expression of F leads to impossible conclusions.

Hence, it seems to me that when we are considering the equilibrium of fluids in the transition layer we must suppose that F depends upon $\frac{\partial\sigma}{\partial x}$, so that the existence of surface tension is itself closely connected to the fact that the system can exist in two phases in contact.

Now suppose that F depends upon σ_x. At first let there be neither cation nor anion in the fluids. In this case our equations are

$$\frac{\partial \mathrm{F}}{\partial \rho_i}=\mathrm{C}_i,\ [i=1, 2, \dots n], \quad . \quad . \quad . \quad . \qquad (20)$$

$$-\mathrm{F}+\sigma_x\frac{\partial \mathrm{F}}{\partial \sigma_x}+\Sigma\rho_i\frac{\partial \mathrm{F}}{\partial \rho_i}=\mathrm{C}_{n+1}, \quad . \quad . \qquad (21)$$

$$\mathrm{D}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (22)$$

where the $n+1$ constants C are to be considered as determinate. A glance at equations (20), (21), (22) shows that the equation determining σ as a function of x is a differential equation of the first order, the constant of integration being determined by the fact that $\sigma=\sigma'$ at P′.

It is more general to suppose that $\frac{\partial \mathrm{F}}{\partial \mathrm{D}}$ does not vanish at P when D=0, and that

$$\Psi_e'-\Psi_e''=\int\frac{\partial \mathrm{F}}{\partial \mathrm{D}}\,dx$$

does not vanish. When $\Psi_e'-\Psi_e''$ does not vanish, the layer of transition may be looked upon as a double sheet of free electricity, but not of real electricity.

Finally, let us suppose that F contains σ_x and that there are electrolytic ions in the fluids. In this case our equations are (15), (17), (18), and (21), and the equation for determining σ as a function of x is a differential equation of the third order, so that σ can satisfy the three boundary conditions that $\Psi_e-\Psi_e'$ and D vanish at P′ and σ becomes σ' at the same point. At the same time $\rho_1, \rho_2, \ldots \rho_n$, D become definite functions of x, and the distance between the two points at which $\frac{\partial\sigma}{\partial x}$ becomes sensibly equal to zero gives the thickness of the transition layer.

. It appears to me at present that the case last mentioned contains the most natural assumptions as to the conception of F, *i. e.* (i.) the fluids are electrolytically dissociated, (ii.) F depends upon $\frac{\partial\sigma}{\partial x}, \frac{\partial\sigma}{\partial y}, \frac{\partial\sigma}{\partial z}$, (iii.) F is sensibly independent of $\frac{\partial\sigma}{\partial x}, \frac{\partial\sigma}{\partial y}, \frac{\partial\sigma}{\partial z}$ when σ becomes either σ' or σ'', although the absence of electrolytic ions does not prevent the existence of the transition layer.

In will be remarked that according to this theory the difference of electric potentials between P′ and P″ is a definite quantity provided that the physical and chemical conditions at P′ are given, and that the condition of the maximum surface tension is quite different from the condition that the difference of electric potentials between P′ and P″ vanishes, so that it is not probable that these two things always occur at the same time.

I shall conclude this paper by giving other expressions of surface tension and by describing the expressions for some quantities relating to it, always neglecting the effect of gravity.

If we write (1) and (4) in the form

$$\frac{\partial \mathrm{F}}{\partial \rho_i}+q_i\Psi_e=\mathrm{C}_i,\ \ [i=1,\, 2,\, \ldots\, n], \quad . \quad . \quad (23)$$

$$-\mathrm{F}+\sigma_x\,\frac{\partial \mathrm{F}}{\partial \sigma_x}+\Sigma\rho_i\,\frac{\partial \mathrm{F}}{\partial \rho_i}=p', \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where p' denotes the pressure at P′, then (8) becomes

$$\mathrm{T}=\int \mathrm{F}dx+p'\int dx-\sum_{i=1}^{i=n}\mathrm{C}_i\int\rho_i\,dx. \quad . \quad . \quad . \quad (25)$$

In the case of only one independent constituent, so called, (25) can be written

$$\begin{aligned}\mathrm{T}&=\int \mathrm{F}dx+p'\int dx-\frac{\partial \mathrm{F}'}{\partial \rho_1'}\int\rho\,dx\\ &=\int\left(\frac{\mathrm{F}+p'}{\rho}-\frac{\mathrm{F}'+p'}{\rho'}\right)\rho\,dx, \quad . \quad . \quad . \quad (26)\end{aligned}$$

where ρ_1' is the density of an electrically neutral constituent at P', and ρ and ρ' the densities at P and P' respectively.

In (23), C_i stands for

$$\frac{\partial F'}{\partial \rho_i'} + q_i \Psi_e',$$

so that C_i contains a term of the form $M\theta + N$, where M and N are arbitrary constants. F contains a term equal to $(M\theta + N)\rho$, so that the right-hand member of (25) is independent of the arbitrary constants M and N. If it were possible to choose the constants M and N so that

$$p' \int dx - \Sigma C_i \int \rho_i dx$$

could be neglected with respect to T for all the possible values of the temperature and densities at P', then (25) would simplify into

$$T = \int F dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

which, I consider, is not a proper expression of T. Equation (27) has apparently the same form as commonly given, but it is different in these respects: F contains $\partial\sigma/\partial x$, and is made up of two terms, the first being equal to

$$\int_0^D E dD$$

and the second being independent of D but a function of $n+3$ variables σ, $\frac{\partial\sigma}{\partial x}$, $\theta, \rho_1, \rho_2, \ldots \rho_n$, where during the integration these $n+3$ variables are to be kept constant.

Next let us find the relation between the temperature coefficient of surface tension and the entropy per unit area

$$H = -\int \frac{\partial F}{\partial \theta} dx, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

the integral being extended from P' to P''.

In the case of one independent constituent, so called, the temperature coefficient of T is definite; but when there are more independent constituents, there is an infinite number of the temperature coefficients according to the different modes of change. Let us take any definite mode of change and denote the corresponding variations by using the symbol d.

By (23), (24), (25), and (28) we have at once

$$\frac{dT}{d\theta} + H = \frac{dp'}{d\theta} \int dx - \Sigma \frac{dC_i}{d\theta} \int \rho_i dx. \quad . \quad . \quad (29)$$

Now take the case of only one independent constituent, so called. Here (29) becomes

$$\frac{d\mathrm{T}}{d\theta}+\mathrm{H}=\frac{dp'}{d\theta}\int dx-\frac{d}{d\theta}\left(\frac{\partial \mathrm{F}'}{\partial \rho_1'}\right)\int \rho\, dx. \quad . \quad . \quad (30)$$

Take the same case and let a unit area of the capillary layer be formed from the first liquid under a constant temperature and in a reversible manner, and let W be the work done on the mass spreading over the unit area of the layer, and Q the quantity of the heat absorbed by the same mass during the change, and U its intrinsic energy. Then it can easily be shown that

$$\mathrm{W}=\mathrm{T}+\frac{p'}{\rho'}\int(\rho-\rho')dx, \quad . \quad . \quad . \quad . \quad (31)$$

$$\frac{\mathrm{Q}}{\theta}=-\frac{d\mathrm{T}}{d\theta}-\frac{1}{\rho'}\frac{dp'}{d\theta}\int(\rho-\rho')dx, \quad . \quad . \quad . \quad . \quad (32)$$

$$\mathrm{U}=u'\int\rho dx+\mathrm{T}-\theta\frac{d\mathrm{T}}{d\theta}+\frac{1}{\rho'}\left(p'-\theta\frac{dp'}{d\theta}\right)\int(\rho-\rho')dx, \quad (33)$$

where u' is the intrinsic energy per unit mass of the fluid at P′. As may be expected, equations (31), (32), and (33) have the same form compared with the case in which the electric field in the layer of transition is not taken into account.

Now consider the case in which there is neither cation nor anion. When the layer is placed in an electric field normal to it, the surface tension T depends upon the electric displacement D′ at P′. By using (6) and observing that the right-hand sides of (20) and (21) are even functions of D′, it is immediately seen that when D′ is infinitely small and the temperature is kept constant during the change,

$$\frac{d\mathrm{T}}{d\mathrm{D}'}=0,$$

which shows that the surface tension is maximum or minimum for D′=0, although, perhaps, $\Psi_e''-\Psi_e'$ does not vanish.

LXXVIII. *A Significant Exception to the Principle of Selection.* *By* PAUL D. FOOTE, *Ph.D.*, F. L. MOHLER, *Ph.D.*, *and* W. F. MEGGERS, *Ph.D.*[*]

[Plate XIII.]

ACCORDING to the Rubinowicz[†] principle of selection, the azimuthal quantum number, in any transition of an electron between two stationary orbits, resulting in radiation, may change by only $+1$, 0, or -1.

Now, in the enhanced lines $\lambda=4686$ and $\lambda\,3203$ emitted by the ionized helium atom, there appear to be certain experimentally observed components which on the basis of the above principle should not exist. Rubinowicz states that the fact that these extra lines have been observed, for which the change in the azimuthal quantum number is 2, obviously[‡] may be attributed to the presence of the electrostatic field exciting the radiation.

While from a consideration of the application of the quantum theory to the Stark effect, and the resulting necessary introduction of a third quantizing process in the mathematical analysis of the lines, Rubinowicz's explanation is consistent with possible fact, it is, of course, by no means a necessary deduction. On the aspherical nucleus theory of Silberstein[§], for example, there should be many more components than would arise with the radially symmetrical (*i.e.* spherical) nucleus assumed in the Rubinowicz theory, and in the more restricted theories of Bohr and Sommerfeld.

A most interesting extension of the quantum theory to the derivation of general spectral series relations, for atoms with several electrons, has been made by Sommerfeld[‖], in which he associates definite azimuthal quantum numbers with the series terms: for example, $n_a=1$ for the *ms* terms, 2 for the *mp* terms, 3 for the *md* terms, and 4 for the *mb* terms. Here, again, exceptions to the principle of selection have been noted and have been attributed to the presence of the exciting electrostatic field, an explanation entirely satisfactory from the mathematical standpoint, if one admits that the lines would not be present in the absence of the field.

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[†] Rubinowicz, *Phys. Zeit.* xix. pp. 441 and 465, 1918. An application of the principle of conservation of moment of momentum to the interaction of æther and matter, in addition to the postulates originally proposed by Bohr.

[‡] *Loc. cit.* p. 466, "handgreiflich."

[§] Silberstein, Proc. Roy. Soc. xcviii, p. 1, 1920.

[‖] Summarized in several chapters of 'Atombau.'

In all the discussions so far published in regard to the failure of the principle of selection, the field referred to has been that applied between the two electrodes of a vacuum tube. The "breaking through" of the principle with helium is a trifle more pronounced in a high voltage capacity discharge than in a lower voltage direct current discharge, supposedly because of the greater field in the former case. It is readily possible, however, to eliminate the effect of such a field in a suitably designed discharge tube. One form of such a tube is illustrated by fig. 1. This consists of a central electrode closely surrounded by a cylindrical net which is similarly enclosed by a cylinder of much larger diameter. The net and outer cylinder are in metallic contact, and the field is applied between the central electrode and net. Thus in the region between the net and cylinder, where the character of the radiation is observed, there exists no applied field. By use of an induction coil or a high voltage transformer very high intensity of radiation is excited, probably sufficient for fine structure analysis.

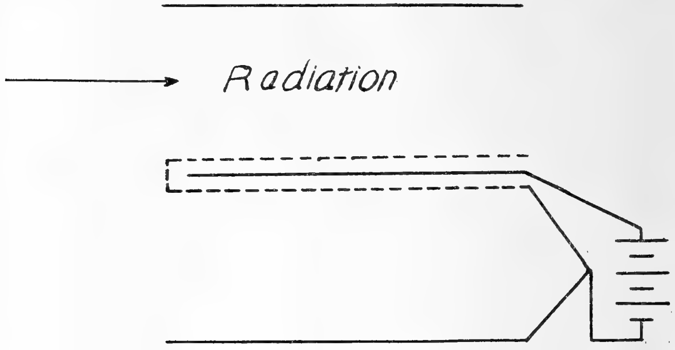

Fig. 1.—Schematic representation of a discharge tube in which the character of the radiation is not disturbed by the exciting electrostatic field.

It is desirable for certain types of work to replace the central electrode by a Wehnelt cathode or heated tungsten filament, in which case the applied field may be reduced to the order of a few volts, to the ionization potential if arc spectra are studied. Currents of 25 amperes and more at 20 volts are readily obtained with hydrogen.

The radiation from such a tube containing potassium vapour is shown in fig. 2 (Pl. XIII.). The total applied field was but 7 volts, and the spectroscope was sighted on the light emitted in the force-free space between the outer electrodes. With a current of 70 milliamperes leaving the filament, the ordinary arc lines (principle, 1st subordinate, 2nd subordinate, Bergmann series) are excited, as shown by the upper spectrogram. On increasing the current to 1000 milliamperes, all other conditions remaining identical, the pair λ 4641 and λ 4642, entirely absent at 70 milliamperes, now become one of the strongest pairs in the spectrum, as shown in the lower half of fig. 2 (Pl. XIII.). These lines have the spectral notation $1s$–$3d$ and are accordingly, if Sommerfeld's interpretation be accepted, the result of an interorbital transition in which the azimuthal quantum number changes by two units. Similar results were obtained with sodium.

The fact that the lines arise when *the exciting field is only* 7 *volts*, and in a location *well shielded electrostatically* from even this small field, makes it extremely doubtful if this and the other above mentioned exceptions to the principle of selection may be attributed to the incipient Stark effect of the applied electrostatic field. The effect in general appears closely related to the magnitude of the current, and might therefore be of a magnetic nature. However, the magnetic effect of a projected beam of electrons should not be large within the beam itself, from which the radiation is observed. A possible explanation may lie in the influence of the electric field of neighbouring ions and electrons, the concentration of which may increase with the current. On the other hand, the explanation may involve a reconsideration of the method whereby single azimuthal quantum numbers have been assigned to each of the s, p, d, and b terms.

Summary.

A new form of discharge tube is described in which the *applied* electrostatic field can exert no influence upon the radiation. Using this tube, the lines $1s$–$3d$ were observed to be one of the most intense pairs in the potassium spectrum, with a current of 1000 milliamperes, while at 70 milliamperes their presence was not detected. The excitation of these lines, for which the change in azimuthal quantum number according to Sommerfeld is two units, is contrary to Rubinowicz's principle of selection as extended by Sommerfeld. It cannot be attributed to the Stark effect of the applied exciting potential. This fact suggests that the extra components in the fine structure of the helium lines likewise may not be called out by the applied field.

In conclusion, the writers desire to express their appreciation for the suggestions made by Dr. L Silberstein, who very kindly read the manuscript.

Bureau of Standards, Nov. 8, 1921.

LXXIX. *A Modified Form of Double Slit Spectrophotometer.*

By A. L. NARAYAN, *M.A.*[*]

[Plate XIV.]

IN different kinds of spectrographic work which have been carried on in the Physical Laboratory of the College, the need for a good spectrophotometer in the visible and ultra-violet regions is keenly felt for the exact location of the absorption centres and for the measurement of their intensity. One of the spectrophotometers adapted to the purpose is the one designed by Vierordt. In this, the collimator is furnished with a double slit in front of which the absorption cell is placed in such a position that the dividing line between the two layers of different thicknesses or the dividing line between the liquid and air coincides with the junction of the two slits. And the slit widths are adjusted until equal illumination is obtained in both the spectra. But the difficulty in the way of regulating the brightness of the spectrum by altering the width of these slits is that it seriously interferes with the purity of the spectrum.

A modified form of double slit spectrophotometer has been devised, which is free from the defects of Vierordt's type. At the same time, it possesses many of the advantages of the sector photometer.

It consists essentially of an electromagnetically maintained pendulum the period of vibration of which is ·5 second nearly, so that it executes 120 oscillations per minute. The bob of the pendulum is a heavy frame of brass containing two rectangular apertures one above the other, there being a well-defined line of demarcation between the two.

Two photographs are given, of which No. 1 shows the photometer and its parts, and No. 2 the photometer in position before the spectrograph.

The widths of both the slits can be adjusted by independent micrometer screws. The whole pendulum is mounted in front of the collimator slit of the spectrograph such that the line of separation between the two slits almost bisects the collimator slit. And the bob of the pendulum can be raised or lowered by a small amount by working a nut by means of which the whole frame constituting the bob is fixed to one end of the pendulum rod.

Since the period of the pendulum is ·5 second, the whole

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[*] Communicated by the Author

length of the pendulum will not be more than 25 to 30 cm., so that the whole arrangement is very compact. Further, by the electromagnet arrangement, the oscillations will have a constant amplitude, and the amplitude also, if necessary, can be varied within certain limits.

It is also possible to produce very small diminution of intensity unlike the case of the sector photometer. It is free from the complications of a motor.

The slit-widths are adjusted so as to get equal illumination in both the spectra. If I′ and I″ are the intensities of the incident and absorbed beams, we have

$$I'' = I' e^{-4\pi k \frac{d}{\lambda}},$$

where k is extinction coefficient, and d the thickness of the layer, so that

$$4\pi k \frac{d}{\lambda} \log e = \log (I'/I'') = \log (b'/b''),$$

where b' and b'' are slit-widths.

Therefore, by knowing b' and b'', k the extinction coefficient can be determined.

Department of Physics,
Maharajah's College, Vizianagram,
10th November, 1921.

LXXX. *Surface Tension of Soap Solutions for Different Concentrations.* *By* A. L. NARAYAN, *M.A.*, *and* G. SUBRAHMANYAM, *B.A.**

[Plate XV.]

THE question of surface tension of soap solutions has from time to time attracted the attention of several scientists, of whom the late Lord Rayleigh was one, who in a series of investigations drew several conclusions of abiding interest. In his paper, "On the tension of recently formed liquid surfaces" (Proc. Roy. Soc. xlvii. pp. 281–287, 1890), Lord Rayleigh, following Marangani, attributed the capability of extension of a soap film into large and tolerably durable laminæ to the "superficial viscosity" due to the presence upon the body of the liquid of a coating or pellicle composed

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* Communicated by the Authors.

of matter whose inherent capillary force is less than that of the mass. In the case of soap, the formation of the pellicle is attributed to the action of atmospheric carbon dioxide liberating the fatty acid from its combination with alkali. This pellicle, Rayleigh remarks, is more akin to a solid than to a liquid.

Since the formation of a coating would be a matter of time, Rayleigh confines himself to this particular aspect of the question, viz., how the surface tension of a soap solution (oleate of soda) changes with the freshness of the surface formed. From observations upon a jet of liquid issuing from an elliptical aperture, he concludes that the addition of a little oleate of soda *does not change* the surface tension if the surface be fresh (Proc. Roy. Soc. xlviii. pp. 127–140, 1890), proving thereby beyond all doubt that the change in the tension is due to external agency. The observations of Dupré (*Théorie Mécanique de la Chaleur,* Paris, 1869, p. 377), and the theory of Prof. W. Gibbs (Connecticut Acad. Trans. vol. iii. pt. 2, 1877–78) lend strong colour to Rayleigh's conclusions.

A strong argument in favour of Marangani's theory is afforded by his observations (Pogg. *Ann.* vol. cxliii. p. 342, 1871) that within very wide limits the superficial tension of soap solutions as determined by capillary tubes is almost independent of strength. In a recent issue of the Journal of Physical Chemistry, vol. xxiv. pp. 617–629 (1920), in the course of a long article on the surface tension of soap solutions, and their emulsifying power, Messrs. M. G. White and J. W. Marden described a series of experiments with the capillary tube, with the result that the surface tension of soap solutions decreases with increase of concentrations, from 49 to 20 and 40 to 21 dynes per centimetre, and that the emulsifying power is closely connected with the surface tension.

As there is wide discrepancy between the results obtained by Lord Rayleigh and others on the one hand and the above authors on the other, the present investigation is taken up with a view to test the accuracy of the results, in which a long series of determinations of the surface tension of soap solutions at different concentrations is made by different methods—strictest possible precautions being observed in maintaining the temperature uniform, and in measuring the various quantities.

Taking advantage of the bubble-forming property of a soap solution, the authors have thought it desirable to measure the surface tension by blowing bubbles, and finding the excess of pressure within the spherical bubbles so formed. This method, besides being more simple and elegant in itself, is free from all assumptions of an uncertain nature, and is one which can very conveniently be applied for an accurate determination of surface tension of soap solutions at different concentrations. The experiment therefore essentially consists in finding the excess of pressure within a spherical bubble, and as this is found to be very small, extreme care is taken to measure it as accurately as possible. This has been effected by a differential micro-manometer, the essential part of which—the bed or the inclined plane, the inclination of which with the horizontal can be varied by an accurately cut micrometer screw—was made by C.S.I. Co., England, and designed to measure angles correct to a micro-radian. The manometer is an almost straight tube of 4 mm. diameter, with its arms making an angle of nearly 180 degrees and having a suitable length of xylene (density 0·850 grm. per c.c. at 28° centigrade) for the manometric liquid, which has been chosen for its extreme mobility and relative involatility. The tube is mounted on a triangular bed of steel resting on a hole-groove-and-point support and hinged about the first two. The platform can be tilted by working a screw having four threads to a mm. and its drum-head divided into 240 equal divisions. It is found by the authors that the whole arrangement far surpasses all other methods of measuring pressure differences both in delicacy and quickness of action.

The manometer is connected to one end of a T-piece, the other ends of which are joined to a compressed air-chamber and a glass tube of 5 mm. diameter respectively. The tube is enclosed in a glass case with sliding doors, and is fed with the minimum quantity of the soap solution. By setting up communication with the compressed air-chamber, a bubble of suitable size is blown. On account of the difference in pressure the manometric column is displaced laterally and the position of the meniscus of the inner end is marked by focussing a comparator, arranged in front of the manometer. When the bubble is off the manometric column resumes its original position and the screw-head is now turned until, as judged by the comparator, the meniscus takes up the same position as when the bubble is on. The readings of the drum before and after the adjustment give the angle of tilt, I, of the foot-board. If l is the length and d the density of the manometric liquid, it is evident that the difference in pressure is $d.g.l \sin I$.

To measure the diameter of the bubble a magnified image of it is projected on a graduated paper placed at a distance. The bubble is illumined with an electric glow-lamp arranged on one side of the glass box, and a good definition of the periphery is secured by making the side of the glass box next to the bulb of a ground glass plate. Some screens are also interposed between the lamp and the glass box, and a preliminary observation with a delicate thermometer indicated no temperature changes within the enclosed space. Without disturbing the position of either the lens or the screen, a translucent scale is held horizontally in the position previously occupied by the bubble, and each of the equal divisions of the graduated paper is calibrated. This avoids the necessity for measuring *u* and *v* and the consequent error in calculating the magnification. This, of course, is done at the conclusion of the experiment.

To make the description clear, a photographic reproduction of the arrangement of the apparatus is given herewith (Pl. XV.).

TABLE I.

Surface Tension of freshly prepared Sodium Oleate Solution.
(By the Bubble method.)

Length of the manometric column...... 9·10 cm.
Density of Xylene (Temp. 28°·1 C.) ... 0·850 grm. per c.c.

Concentration.	No. of rotations of the micrometer screw.	Diameter (to be multiplied by 3/5·35).	Surface Tension. (Dynes per cm.)
Saturated solution.	11 97	3·35 cm.	23·50
0·667 of ,,	10 108	3·66 ,,	23·53
0·445 ,,	11 27	3·47 ,,	23·71
0·297 ,,	12 25	3·12 ,,	23·23
0·198 ,,	10 57	3·60 ,,	23·19
0·132 ,,	11 82	3·33 ,,	23·23
0·088 ,,	11 33	3·44 ,,	23·57
0·059 ,,	12 66	3·10 ,,	23·41
0·039 ,,	12 58	3·12 ,,	23·50
Length of the manometric column: 9·00 cm. Other data precisely the same.			
0·0909 ,,	11 83	3·38 cm.	23·33
0·0625 ,,	11 199	3·26 ,,	23·46
0·0476 ,,	12 130	3·07 ,,	23·42
0·0385 ,,	12 179	2·98 ,,	23·11
0·0322 ,,	No bubbles could be blown.		

Table II.

Surface Tension of Castyl Soap Solution used for Water Analysis.

(By the Bubble method.)

Length of the Manometric column...... 9·40 c.m.

Concentration.	No. of rotations of the micrometer screw.	Diameter (to be multiplied by 5/5·70).	Surface Tension. (Dynes per cm.)
Saturated solution.	13 121	3·00 cm.	23·66
0·5 of ,,	13 185	2·93 ,,	23·61
0·33 ,,	13 00	3·09 ,,	23·52

Length of the manometric column: 9·75 cm.

		Diameter (to be multiplied by 3/5·34).	
0·25 ,,	12 189	2·86 cm.	23·70
0·17 ,,	12 69	2·96 ,,	23·57
0·090 ,,	12 237	2·80 ,,	23·57
0·062 ,,	15 87	2·38 ,,	23·69
0·048 ,,	14 71	2·55 ,,	23·62
0·038 ,,	14 236	2·47 ,,	23·98
0·032 ,,	15 46	2·40 ,,	23·62
0·028 ,,	16 45	2·31 ,,	24·23
0·024 ,,	16 45	2·31 ,,	24·23

For further dilutions no bubbles could be formed.

To compare the values thus obtained with those by the capillarity method, the surface tension for the same concentrations has been determined by the capillarity method. Most of the tubes to be ordinarily met with have been discarded for want of a perfectly uniform and circular bore. For this purpose, the stem of a broken thermometer is found to answer excellently well, notwithstanding the elliptical nature of the bore. If $2a$ and $2b$ are the major and minor axes, the area of the section of the bore is evidently πab, and the perimeter

$$4\int_0^{\frac{\pi}{2}} (a^2 \sin^2 \phi - b^2 \cos^2 \phi)^{\frac{1}{2}} d\phi$$

$$= 4a\int_0^{\frac{\pi}{2}} (1 - e^2 \cos^2 \phi)^{\frac{1}{2}} d\phi,$$

where of course e is the eccentricity defined by

$$e^2 = \frac{a^2 - b^2}{a^2}$$

$$= 4a \cdot \frac{\pi}{2} \left\{ 1 - \tfrac{1}{2} e \frac{2\mathrm{C}_1}{2^2} + \frac{\frac{1}{2}(\frac{1}{2}-1)}{2\,!} \cdot e^4 \cdot \frac{4\mathrm{C}_2}{2^4} \right.$$
$$\left. - \frac{\frac{1}{2}(\frac{1}{2}-1)(\frac{1}{2}-2)}{3\,!} \cdot e^6 \cdot \frac{6\mathrm{C}_3}{2^6} + \ldots \right\},$$

which in the present case, as e is smaller than l, is a rapidly converging series and can be calculated to the desired degree of approximation.

Some readings have, however, been taken with a few capillary tubes having very nearly a circular bore. In the case of such tubes, correction for the weight of the liquid above the bottom of the meniscus in the capillary tube is applied according to Hagen & Desain's formula

$$h = h_0 + \frac{a^2 r}{3a^2 + r^2},$$

where a^2 is the capillary constant, h_0 and h are observed and corrected heights.

The height of the liquid column and the diameter of the tube are measured in all these cases by a comparator (reading to hundredths of a mm.), for which we are indebted to the C.S.I. Co., England. The following observations (Tables III. to V.) are the mean of a number of readings, which, from considerations of space, we could not give in detail. Before each set of measurements the tubes are thoroughly cleaned by a hot mixture of nitric and chromic acids and washed well in plenty of running tap-water, and finally dried in a current of warm air.

(In preparing the solutions, excess of soap is at first taken, and is dissolved in water. The solution is then allowed to settle, and the clear liquid decanted into a beaker. It is then filtered twice. One hundred c.c. of this filtered solution is successively diluted with 100, 200, 300, 400, ... c.c. of water. Hence the concentrations are expressed in terms of the saturated solution.)

It will be seen that the surface tension in all these cases never differs much from 23·5 dynes per cm. (Temp. 29°·1 C.), and is about the same as Lord Rayleigh's results, whose values range between 25·3 and 24·6 dynes per cm. (Temp. 18°) ("On the tension of water surfaces, clean and contaminated, investigated by the method of ripples" (Phil. Mag. xxx. pp. 386–400, November 1890).

TABLE III.

Sodium Oleate Solution: with capillary tube with an elliptical bore.

$2a = 0·0255$. $2b = 0·0178$ cm.

Concentration.	Height (corrected).	Surface Tension. (Dynes per cm.)
Saturated solution.	4·658 cm.	22·57
0·5 of ,,	4·707 ,,	22·70
0·33 ,,	4·74 ,,	22·88
0·25 ,,	4·783 ,,	23·00
0·17 ,,	4·917 ,,	23·63
0·090 ,,	4·908 ,,	25·57
0·062 ,,	4·999 ,,	23·93
0·048 ,,	5·080 ,,	24·38
0·038 ,,	5·182 ,,	24·83
0·032 ,,	5·048 ,,	24·23
0·028 ,,	5·000 ,,	24·00

TABLE IV.

Castyl Soap Solution: by a capillary tube with an elliptical bore.

Concentration.	Height (corrected).	Surface Tension. (Dynes per cm.)
Saturated solution.	5·038 cm.	24·27
0·5 of ,,	4·949 ,,	23·85
0·33 ,,	4·894 ,,	23·59
0·25 ,,	4·906 ,,	23·64
0·17 ,,	4·874 ,,	23·49
0·090 ,,	4·873 ,,	23·49
0·062 ,,	4·964 ,,	23·92
0·048 ,,	4·934 ,,	23·78
0·038 ,,	4·923 ,,	23·73
0·032 ,,	4·894 ,,	23·59

TABLE V.

Castyl Soap Solution: by different capillary tubes with circular bore.

Diameter of Bore. (cm.)	Corrected Height. (cm.)	Surface Tension. (Dynes per cm.)
0·029	3·398	24·10
0·020	4·796	23·49
0·0320	3·164	24·70

In order to examine how the surface tension of soap solutions varies with dilution at great dilutions, we have thought it desirable to institute another series of experiments with soap solutions. As no bubbles could be blown at these great dilutions, *i. e.* below 0·22 gm. per 100 c.c. of solution, in all these experiments measurements of surface tension are made by the capillary tube method with the tubes used in the former experiments.

TABLE VI.

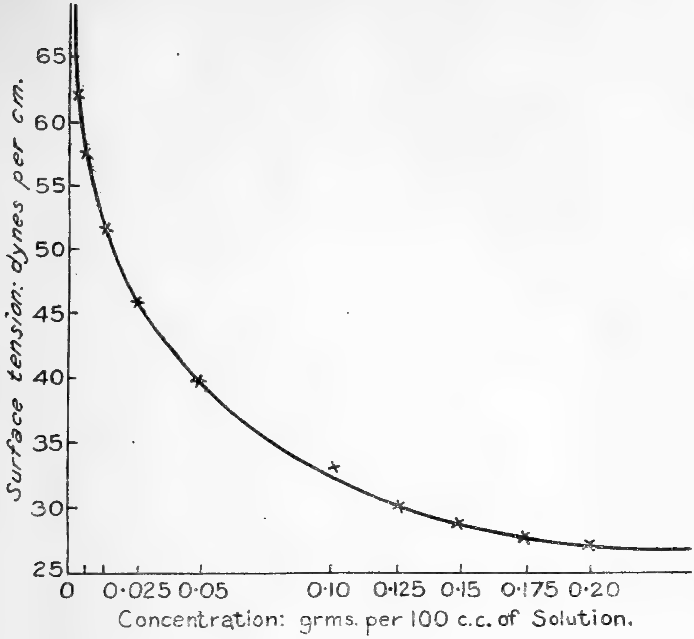
Castyl Soap Solution: Surface Tension for different concentrations (at great dilutions).

Concentration—Gms. per 100 c.c. of solution.	Height (corrected).	Surface Tension. (Dynes per cm.)
0·20	5·44 cm.	27·10
0·175	5·557 ,,	27·70
0·150	5·768 ,,	28·70
0·125	6·015 ,,	29·90
0 100	6·653 ,,	33·10
0·050	8·025 ,,	40·09
0·025	9·212 ,,	45·91
0·0125	10·525 ,,	52·36
0·0062	11·47 ,,	57·03
0 0031	12·475 ,,	61 940
0·00155	13·02 ,,	64 71

It will be seen from comparison of the observations recorded here with those already recorded, that the surface tension of soap solution begins to increase with dilution only at great dilutions, up to 0·23 grm. per 100 c.c. of solution, the surface tension being practically constant, and then rapidly rising with dilution.

The results of the experiments are graphically represented on the diagram, where concentrations in grams per 100 c.c. of solution are plotted along the X-axis, and the surface tension values along the Y-axis. The curve, which may well be styled the isothermal of Castyl soap solution at 28° C., is an hyperbola. Further experiments are in progress—

(i.) to construct the isothermals of different soap solutions;
(ii.) to construct the isothermals of one and the same soap (Castyl soap) for different temperatures from 30° to 100° C.



Conclusions.

(1) These experiments place beyond all doubt the fact that the surface tension of soap solutions is the same for all concentrations between very wide limits.

(2) They further lend weight to the reliability of the bubble method for studying the surface tension of soap solutions although the apparatus is seemingly more complex than that for the capillarity method.

(3) The close agreement between the results obtained by the soap-bubble method and those obtained by the capillarity method further shows that the angle of contact in this case is 0, as has also been conclusively established by the experiments of Bosanquet and Hartley (Phil. Mag. vol. xlii. Sept. 1921) and Richards and Caver (Journal American Chemical Society, 1921, p. 827).

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Maharajah's College, Vizianagram,
15th November, 1921.

LXXXI. *On the Kinetic Theory of Solids (Metals) and the Partition of Thermal Energy.*—Part I. *By* B. M. Sen, *Dacca College, Dacca, Bengal*[*].

Preface.

THE Kinetic Theory of Gases has been developed in great detail, but hardly any progress has been made with that of the solids. In the absence of any such well-developed theory, attempts are sometimes made to apply the results of the Kinetic Theory of Gases to the case of solids, as, for example, in the theory of electric conduction. The results can hardly be regarded as satisfactory. One fundamental assumption of the Gas-theory is that the volume of the molecules is negligible in comparison with that of the gas itself. Clearly, this does not hold good even approximately for solids. Lately Nernst and others have approached the subject from the standpoint of Planck's Quantum Theory. In the present paper an attempt has been made to develop the theory for metals on the basis of classical mechanics.

It is known that for 1° rise of temperature, every atom of any metal absorbs 4×10^{-16} erg in round numbers. On the principle of equi-partition of energy, every atom having three degrees of freedom of translation, this is explained by the supposition that the translational motion absorbs one-half of this quantity of energy

$$[\tfrac{1}{2}mv^2=\alpha\theta, \text{ where } \alpha=2{\cdot}02\times10^{-16}],$$

and the other half is absorbed by the increase of potential energy of vibration, whose mean value is the same as that of the kinetic energy. But there are difficulties in the way, as the specific heat increases gradually, whereas the degrees of freedom can increase only by leaps[†]. It may be pointed out that Born[‡] and others have developed the theory of crystal lattices, which gives the twenty-one constants required by the mathematical theory of elasticity. Between two neighbouring molecules there must be a force of attraction and another of repulsion which keep the molecules at their proper distance. Born assumed the form $a/r+b/r^n$ for the mutual potential energy, the first term representing the force of attraction and the second repulsion. But this does

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[*] Communicated by the Author.

[†] MacLewis, 'Physical Chemistry,' vol. ii. p. 29.

[‡] Born, *Dynamik der Kristalgitter, Aufbau der Materie,* where full references are given.

not easily explain the heat expansion of the body. If heat be a form of motion, it is clear that the motion of the atoms must have something to do with the force of repulsion. I have, therefore, assumed that the repulsion is of the nature of an impulse due to what are called impacts in the Kinetic Theory of Gases. The problem thus becomes a dynamical one and the mathematics much more difficult.

Again, in order to allow impacts, it is necessary to assume that the mutual distances of molecules are not large enough for free vibration. For simplicity I have assumed that the amplitude is small in comparison with the atomic dimensions. The results obtained completely bear out with the assumption.

It may be pointed out that the phraseology used is that of the Kinetic Theory of Gases. Use has, therefore, been made of terms such as impacts, radius of atoms, which in the light of modern researches on the structure of matter will have to be accepted in a generalized sense.

The numerical values have been taken from Kaye and Laby.

1. *Some numerical values.*

Let N be the number of molecules in a metal supposed monatomic per c.cm., and l the average distance between the centres of two adjacent ones. Then $Nl^3=1$ *.

The number of molecules of gas per c.cm. at N.T.P.

$$=2{\cdot}75\times10^{19}.$$

Let W be the atomic weight, and D the density of the metal. Let w be the weight of one molecule of the standard gas (O=16).

Then

$$D=\text{wt. of 1 c.cm. of the metal}=N.W.\tfrac{1}{2}w.$$

$$\text{wt. of 1 c.cm. of oxygen}=2{\cdot}75\times10^{19}\times16w=1{\cdot}429\times10^{-3}.$$

$$\therefore\ \frac{NW}{D}=6{\cdot}16\times10^{23}$$

$=$the number of atoms in one gram atom of the metal $=\epsilon$ say.

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* Strictly speaking this relation holds only for the cubical arrangement of the molecules. But for the face-centred cubical arrangement the equation ought to be $Nl^3=\sqrt{2}$. This would increase the value of l given in the table by about 11 per cent. But there will be no occasion to use the arithmetical values of l. All that we need trouble about is the order of magnitude of l.

TABLE I.

Metals.	Density D.	Atomic weight.	N.	l.	M. wt. of mol.	α_1 coeff. of expansion.	c compressibility.
Cu......	8·93	63·57	$8·64 \times 10^{22}$	$2·26 \times 10^{-8}$	$1·03 \times 10^{-22}$	$16·7 \times 10^{-6}$	$·74 \times 10^{-12}$
Ag......	10·5	107·9	5·97 ,,	2·55 ,,	1·75 ,,	18·8 ,,	·92 ,,
Fe......	7·86	55·84	8·67 ,,	2·26 ,,	0·91 ,,	10·2 ,,	·63 ,,
Zn......	7·1	65·37	6·69 ,,	2·46 ,,	1·06 ,,	26 ,,	
Pb......	11·37	207·2	3·38 ,,	3·09 ,,	3·36 ,,	27·6 ,,	2·0 ,,
Au ...	19·32	197·2	6·05 ,,	2·55 ,,	3·19 ,,	13·9 ,,	0·60 ,,
Pt......	21·50	195·2	6·78 ,,	2·45 ,,	3·17 ,,	8·9 ,,	0·41 ,,
Sn......	7·29	118·7	3·78 ,,	2·98 ,,	1·93 ,,	21·4 ,,	1·9 ,,
Al......	2·7	27·1	6·16 ,,	2·53 ,,	0·44 ,,	25·5 ,,	1·33 ,,

2. *Arrangement of molecules in an isotropic body.*

To find the number of molecules which can be arranged about a central one at a distance l from it and from one another. The problem is the same as the determination of the number of tetrahedrons having all their edges equal to l and having one vertex at the centre which can be fitted inside a sphere of radius l. For every tetrahedron we have an equilateral triangle of side l having its vertices on the sphere. If a, b, c be the sides of the spherical triangle so formed,

$$a=b=c=60^\circ.$$

$$\therefore \text{ Cos A}=\tfrac{1}{3}, \quad \text{and} \quad \text{A}=70^\circ.$$

$\therefore$ the spherical excess $=30^\circ$.

The total number of tetrahedrons $=\dfrac{4\pi}{\pi/6}=24$.

For each tetrahedron there are three molecules and each molecule comes in $\dfrac{360}{70}$, or about five times. The number of molecules, therefore, is about 14.

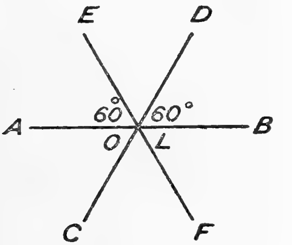
3. *Rough working model.*

It is not geometrically possible to have an arrangement of molecules on a sphere so that the spherical arc between any two adjacent ones is 60°. But in a rough model form these 14 may be supposed to be arranged as follows :—The centres all lie on a sphere of radius l. Two may be placed at the two poles which may be arbitrarily chosen. Three meridian circles are drawn making an angle of 60° with each other. On each of these, beside the two at the poles, are placed four others, one at each extremity of a pair of diameters making an angle of 60° with the axis. There are thus six molecules on each of these meridian circles, one at each vertex of a regular hexagon inscribed in the circle. This arrangement gives the 14 molecules arranged about the central one. It is symmetrical through the centre and has an axis.

4. *The Potential Energy of displacement.*

Let us consider the motion of a molecule O in the direction AB which we take as the direction of the axis of the model (fig. 1). Let two molecules be placed at A and B and let

Fig. 1.



C, D, E, F be the four other molecules in the same meridian plane, so that $OA=OB=OC=AE\ldots=l$. For simplicity, we shall assume that the central one is the only one vibrating, the others being stationary in their mean positions. Let L be the extreme position of O. Take $OL=a$, and $r=$the radius of the molecule. Then

$$l=a+2r.$$

Let $f(l)$ be the potential energy of two molecules at a distance l. Then for a displacement x taken small, along the axis of the model, the potential energy due to A and B is

$$f(l+x)+f(l-x)=2f(l)+x^2f''(l).$$

The potential energy due to a pair like C, D

$$=f(r_1)+f(r_2) \text{ where } r_1=CL, \text{ and } r_2=DL.$$

Now $$r_1^2=l^2+x^2+xl.$$

$$\therefore\quad r_1=l+\tfrac{1}{2}x+\tfrac{3}{8}\cdot\frac{x^2}{l},$$

neglecting higher powers of x,

and
$$r_2 = l - \tfrac{1}{2}x + \tfrac{3}{8} \cdot \frac{x^2}{l} .$$

$$\therefore \quad f(r_1) = f(l) + \left(\tfrac{1}{2}x + \tfrac{3}{8}\frac{x^2}{l}\right) f'(l) + \tfrac{1}{8}x^2 f''(l),$$

$$\text{and} \quad f(r_2) = f(l) + \left(-\tfrac{1}{2}x + \tfrac{3}{8}\frac{x^2}{l}\right) f'(l) + \tfrac{1}{8}x^2 f''(l).$$

$$\therefore \quad f(r_1) + f(r_2) = 2f(l) + \tfrac{3}{4}\frac{x^2}{l} f'(l) + \tfrac{1}{4}x^2 . f''(l).$$

There are six pairs of such molecules. The total potential energy

$$= 14f(l) + \tfrac{1}{2}x^2 \left\{ \frac{9f'(l)}{l} + 5f''(l) \right\} .$$

It may be noted that the attractive force is $f'(l)$. And if, as is only natural to assume, the force diminishes with the distance, $f''(l)$ is negative. And if the force varies as any power of the distance, the two terms of the variable part of the potential energy are of the same order of magnitude.

It is obvious, moreover, from general considerations that the potential energy for any displacement x must be of the type $A + Bx^2 + \ldots.$ If the coefficient of x be not zero, there will be a permanent force independent of the displacement.

The equation of energy, therefore, is

$$MV^2 + x^2 \left\{ \frac{9f'(l)}{l} + 5f''(l) \right\} = \text{const.} \quad . \quad . \quad (1)$$

The motion, therefore, is simple harmonic if the coefficient of x^2 be positive. If the molecule can complete its oscillation, the average potential energy would be equal to the average kinetic energy. We assume that this is not the case, so that the molecule comes into collision with its neighbour as soon as it has described a small fraction of its path *.

5. *Order of magnitude of the Kinetic and Potential Energy terms.*

In the equation (1) above, the first term

$$MV^2 = 2\alpha\theta$$

is of order 10^{-14}, for $\alpha = 2{\cdot}02 \times 10^{-16}$ and θ is the temperature. From known values of the specific heat and the coefficient of linear expansion, it will be proved that $f'(l)$ is of order 10^{-5} and the maximum displacement of order 10^{-10}. Now, l being of order 10^{-8}, the potential energy term is of order

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* The reason for this assumption has been given in the preface.

10^{-17}. The error in neglecting it is therefore small. Its effect is felt at the boundary where it gives rise to a powerful surface pressure.

We neglect, therefore, the change in the potential energy and take the velocity as constant throughout the motion. Also we neglect the duration of the impact in comparison with the period of vibration. If t_1 be the time from one extreme position to the other, and t_2 the duration of the impact, t_2 will be neglected in comparison with t_1 [*].

6. *Heat Relations.*

To consider the heat relations of a body it is necessary to formulate a relation between the molecular kinetic energy and the temperature of the body. It may be pointed out that the equation

$$\tfrac{1}{2}\mathrm{MV}^2=\alpha\theta$$

for gases does not follow from dynamical considerations, but is a direct consequence of Boyle and Charles' law. As a matter of fact, we may take it as the definition of temperature. For a solid we take

Q = the average external kinetic energy of a molecule $=\tfrac{1}{2}\mathrm{MV}^2$.

P = the internal kinetic energy per molecule, *i. e.* the energy of motion relative to the centre. These are, of course, additive in the ordinary way.

If Q be an analytic function of θ vanishing with it, we may take

$$\mathrm{Q}=\alpha\theta+\alpha_1\theta^2+\ldots.$$

We shall follow the usage of the Gas-theory and suppose that the temperature is determined by the average external kinetic energy of the molecule, taking

$$\mathrm{Q}=\alpha\theta.$$

7. *Partition of Energy.*

When the temperature of a solid is raised by 1° C., the quantity of energy absorbed per unit volume is $\mathrm{D}s\mathrm{J}$, s being the specific heat and $\mathrm{J}=4\cdot18\times10^7$ ergs. Now Dulong and Petit's law states that $\mathrm{W}s$ is approximately constant for all elements. Energy imparted to every molecule

$$=\frac{\mathrm{D}s\mathrm{J}}{\mathrm{N}}=\frac{\mathrm{W}s}{\epsilon}.\mathrm{J}.$$

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[*] *Cf.* J. J. Thomson, 'Corpuscular Theory of Matter,' p. 93.

For a gas such as oxygen,

$$c_p = \cdot 24, \quad \gamma = 1\cdot 4 ;$$

$$\therefore \quad c_v = \frac{\cdot 24}{1\cdot 4}.$$

Energy absorbed by each molecule for 1° rise of temperature

$$= \frac{D}{N} c_v J = 3\cdot 74 \times 10^{-16},$$

whereas the external kinetic energy is increased by

$$\alpha = 2\cdot 02 \times 10^{-16}.$$

In the Kinetic Theory of Gases this difference is explained by the diatomic nature of the molecules, there being no intermolecular forces*. A portion may also be accounted for by the absorption by the electrons. But for solids the matter is complicated by the presence of intermolecular forces against which work has to be done by the heat expansion.

For a solid we assume that the total energy imparted is split up into three portions :—

(1) a quantity α absorbed in increasing the external kinetic energy $Q = \frac{1}{2} MV^2 = \alpha\theta$, where $\alpha = 2\cdot 02 \times 10^{-16}$, and θ the temperature.

(2) a quantity B absorbed in increasing the kinetic energy of rotation relative to the centre. This is presumably absorbed by the electrons in the outer rings. We take

$$P = A + B\theta = \tfrac{1}{2} n \,.\, mv^2,$$

where A represents the store of energy, n the number of electrons taking part in the absorption, m the mass of an electron for velocities small in comparison with that of light, and v the velocity.

(3) a quantity β absorbed in increasing the potential energy of the molecules, *i. e.* in doing work against the inter-molecular forces.

$$\therefore \quad \alpha + \beta + B = \frac{Ws}{\epsilon} J.$$

Taking $\frac{1}{2} MV^2 = \alpha\theta$ for Cu at $\theta = 17°$ C.,

$$V = 3\cdot 7 \times 10^4.$$

Thus for metals at ordinary temperatures V is of order 10^4. A table of values is given for solids and gases. It may

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* Jeans, 'Dynamical Theory of Gases,' art. 270.

be noted that at first sight the similarity in the values of the total gain of energy for solids and gases may tempt one to apply the diatomic explanation to solids. But the value of N has been calculated on the monatomic basis. If the molecules be taken as diatomic the numbers in the third column will be doubled and the similarity will disappear.

Total gain of energy per molecule for 1° C.

$$= s\mathrm{W} \times 6{\cdot}8 \times 10^{-17}.$$

TABLE II.

Metals.	Specific heat.	Atomic weight.	Total gain of energy per mol.	$\beta+\mathrm{B}$.	β (art. 9).	F (art. 9).
Cu......	·09	63	3·87 × 10^{-16}	1·85 × 10^{-16}	·76 × 10^{-16}	1·1 × 10^{-5}
Ag......	·053	108	3·89 ,,	1·87 ,,	1·03 ,,	1·13 ,,
Au......	·03	197	4·02 ,,	2	·84 ,,	1·25 ,,
Pt......	·031	195	4·11 ,,	2·09 ,,	·61 ,,	1·47 ,,
Fe.. ...	·1	56	3·81 ,,	1·8 ,,	·50 ,,	1·14 ,,
Pb......	·03	207	4·22 ,,	2·2 ,,	1·22 ,,	0·6 ,,
Sn......	·05	119	4·04 ,,	2	·78 ,,	1
Zn......	·09	65	3·98 ,,	1·96 ,,	...	...
Gases.	C_v.	Density.				
A	·0746	...	1·976 × 10^{-16}			
H	2·40	0·09 × 10^{-3}	3·27 ,,			
N	·175	1·25 ,,	3·34 ,,			
O	·17	1·43 ,,	3·70 ,,			
CO ...	·17	1·25 ,,	3·23 ,,			
CO_2 ...	·165	1·976 ,,	4·96 ,,			

8. *The Amplitude of Molecular Vibration* a.

We revert to the consideration of a vibrating molecule O surrounded by fourteen others stationary in their mean positions. Its average velocity in any direction may be taken to be $\mathrm{V}/\sqrt{3}$. At each collision this forward velocity is reversed. Thus there is a change of momentum at the point $2\mathrm{MV}/\sqrt{3}$ at each collision, or $\dfrac{\mathrm{MV}}{\sqrt{3}(t_1+t_2)}$ per sec., $2(t_1+t_2)$ being the period of vibration. Neglecting t_2 the duration of the collision, and putting $t_1=2\sqrt{3}a/\mathrm{V}$, the change of momentum becomes $\dfrac{\mathrm{MV}^2}{6a}=\dfrac{\alpha\theta}{3a}$. There being $\mathrm{N}^{2/3}$ molecules per sq. cm., the pressure at the surface within the mass of the metal is $\mathrm{N}^{2/3}\cdot\dfrac{\alpha\theta}{3a}$ per sq. cm.

We now calculate the pressure at the surface due to the molecular forces, the atmospheric pressure being of course negligible. We take into account only seven of the fourteen molecules lying on one side of the equatorial plane. The potential energy in the displaced position, x being the displacement from the mean position,

$$=f(l-x)+6f(l-\tfrac{1}{2}x)$$
$$=7f(l)-4xf'(l).$$

Force along the normal

$$=4f'(l)=4\mathrm{F},$$

where F is the force between two molecules.

Pressure at the surface $=4\mathrm{N}^{2/3}\,.\,\mathrm{F}$.

$$\therefore\quad \frac{\alpha\theta}{3a}=4\mathrm{F}$$

$$\text{or}\qquad a=\frac{\alpha\theta}{12\,\mathrm{F}}\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

9. *Compressibility.*

We proceed to find the simplest of the elastic constants, viz. compressibility, on the basis of our hypothesis. The work done against the molecular forces $=\beta$ per molecule for 1° rise of temperature.

Now the pressure at the surface $=4\mathrm{F}\,.\,\mathrm{N}^{2/3}$.

Work done against the surface pressure $=\mathrm{N}^{2/3}\,.\,12\mathrm{F}\alpha_1$, where α_1 is the coefficient of linear expansion.

Work done against the inter-molecular forces per unit volume $=7\mathrm{F}\delta l\,.\,\mathrm{N}=7\mathrm{F}\alpha_1\mathrm{N}^{2/3}$, there being fourteen molecules arranged about each individual molecule and $\delta a=\delta l$.

$$\therefore\quad \mathrm{N}\beta=19\mathrm{F}\alpha_1\mathrm{N}^{2/3}.\quad\therefore\quad \mathrm{F}=\frac{\beta}{19\alpha_1 l}\,. \quad . \quad . \quad . \qquad (3)$$

$$\therefore\qquad a=\frac{\alpha\theta}{12\mathrm{F}}=\frac{19\alpha\theta\,.\,\alpha_1 l}{12\beta}\,.$$

Now the surface pressure $=4\mathrm{F}\,.\,\mathrm{N}^{2/3}=\dfrac{4\mathrm{N}\beta}{19\alpha_1}$.

If the pressure be increased by one dyne without change of temperature, it increases by $\dfrac{19\alpha_1}{4\mathrm{N}\beta}$th part of itself.

$$\therefore\quad \frac{\delta a}{a}=-\frac{19\alpha_1}{4\mathrm{N}\beta}.$$

$$\therefore\quad \frac{\delta l}{l}=-\frac{a}{l}\cdot\frac{19\alpha_1}{4\mathrm{N}\beta}\,.$$

$$\text{Compressibility } C=\frac{57\alpha_1 a}{4N\beta l}=\frac{57\alpha_1}{4N\beta l}\times\frac{19\alpha\theta}{12\beta}\alpha_1 l.$$

$$\therefore\quad \beta^2=\frac{19\times19\times\alpha_1{}^2}{16CN}\alpha\theta \quad\text{or}\quad \beta=\frac{19}{4}\alpha_1\sqrt{\frac{\alpha\theta}{CN}}. \quad . \quad (4)$$

Taking $C=\cdot74\times10^{-12}$ and $\theta=17^\circ$ C.,

we get $\beta=\cdot76\times10^{-16}$ for Cu.

Substituting this value of β, we have for Cu

$$F=1\cdot1\times10^{-5} \text{ and } a=4\cdot4\times10^{-10}.$$

The value of β for the different metals has been calculated and shown in the second table. The values of B are obtained by difference.

10. The calculation of Young's modulus gives good support to the previous work. Suppose that the body is stretched so that l increases by x.

$$\therefore\quad \delta l=\delta a=x, \text{ where } l=a+2r.$$

Putting $a+x$ instead of a in art. 8, the half-period of vibration

$$t_1=2\sqrt{3}(a+x)/V.$$

The change of momentum per sec. is, therefore,

$$\frac{MV^2}{6(a+x)}=\frac{MV^2}{6a}\left(1-\frac{x}{a}\right).$$

The force of repulsion due to impacts is diminished by $\frac{MV^2x}{6a^2}$.

The force of attraction

$$=f'(l+x)-f'(l)+xf''(l),$$

$f''(l)$ being of course negative.

The total change in the force of attraction per molecule

$$=x\left\{\frac{MV^2}{6a^2}+f''(l)\right\},$$

and the total change per unit area

$$=xN^{2/3}\cdot\left\{\frac{MV^2}{6a^2}+f''(l)\right\}.$$

Now the extension is x/l. Young's modulus is, therefore,

$$N^{2/3}\cdot l\left\{\frac{MV^2}{6a^2}+f''(l)\right\}=\frac{1}{l}\left\{\frac{MV^2}{6a^2}+f''(l)\right\}.$$

It is known that the value of Young's modulus for the common metals is of the order 10^{12}. Taking the case of Cu by way of illustration, the first term $=5\times 10^{12}$ roughly.

The experimental value $=1{\cdot}23\times 10^{12}$.

$\therefore \ \frac{1}{l}f''(l)$ is of order 10^{12}, which makes $f''(l)$ of order 10^4.

The potential energy term in the equation of energy in art. 4 is therefore of order 10^{-16}.

11. *Residual Rays.*

We can make a rough calculation of the frequency of vibration of the molecules at the surface. We know that for a Cu molecule,

$$\begin{array}{lccl} \text{V is of order} & & & 10^4, \\ \text{M} & ,, & ,, & 10^{-22}, \\ \text{F} & ,, & ,, & 10^{-5}. \end{array}$$

Neglecting the variations of the force, the frequency $\nu=\frac{\text{F}}{2\text{MV}}$, which is of order 10^{12}.

This agrees with the experimental values *.

12. *Conclusion.*

We have, therefore, arrived at a consistent theory of the solid state. Starting from known values of the specific heat, compressibility, and the coefficient of linear expansion, we have investigated the amplitude of molecular vibration and the inter-molecular forces. The partition of the gain of thermal energy has been dealt with. We have found that for Cu, for example,

(1) $2{\cdot}02\times 10^{-16}$ erg is absorbed by each molecule to increase the energy of translational motion,

(2) $1{\cdot}2\times 10^{-16}$ erg is absorbed by the rotational motion, and presumably increases the energy of the electrons,

(3) $\cdot 76\times 10^{-16}$ erg is absorbed in doing work against the inter-molecular forces.

The cases of cubical and face-centred cubical crystals have been dealt with in the next paper ; the results obtained do not differ materially from those obtained here.

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* McLewis, 'Physical Chemistry,' vol. ii. p. 58.

LXXXII. *On the Kinetic Theory of Solids (Metals) and the Partition of Thermal Energy.*—Part II. *By* B. M. Sen, *Dacca College, Dacca, Bengal* [*].

Preface.

In my previous paper on the "Kinetic Theory of Solids (Metals)," Part I.[†], I investigated the theory of the solid state with a rough working model of fourteen molecules placed on a sphere about each individual molecule at the centre. The idea was to make the distance between any two adjacent molecules equal to the radius of the sphere (the body being isotropic) so that the spherical distance between them is 60°. This is geometrically impossible, but the model satisfies this condition approximately together with the condition of symmetry.

In the present paper, I have restated the theory for the cubic and face-centred cubic crystals. These are the two arrangements which are common for the solid state. The arguments have been put briefly. For a more detailed statement the reader is referred to the previous paper.

1. *Potential energy of displacement.*

Let us suppose that six molecules are placed at a distance l from the central molecule, two on each axis. Let the components of the displacement of the central molecule be x, y, z, the others being fixed in their mean positions. Then the potential energy for the displacement x

(1) due to the molecules on the x-axis

$$=f(l+x)+f(l-x)=2f(l)+x^2f''(l),$$

(2) due to the pair of molecules on the y-axis

$$2f\left(l+\frac{1}{2}\frac{x^2}{l}\right)=2f(l)+\frac{x^2}{l}f''(l),$$

(3) due to the pair of molecules on the z-axis

$$2f(l)+\frac{x^2}{l}f''(l).$$

The combined effect of these six molecules for the general displacement

$$=6f(l)+a^2\left\{\frac{2}{l}f'(l)+f''(l)\right\}, \quad \text{where } a^2=x^2+y^2+z^2$$

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[*] Communicated by the Author.

[†] *Suvra*, p. 672.

The equation of energy is, therefore,

$$\tfrac{1}{2}\mathrm{MV}^2+a^2\left\{\frac{2}{l}f'(l)+f''(l)\right\}=\text{const.}$$

If the molecule were at liberty to swing to its natural amplitude, the mean kinetic energy would be equal to its mean potential energy. We make the assumption that this is not the case, the vibrating molecule coming into collision with the adjacent one before reaching the extreme position of the natural vibration *.

2. *Amplitude of molecular vibration.*

At each collision the forward motion is reversed, so that there is a change of momentum at the point $=2\mathrm{MV}/\sqrt{3}$ at each collision, or $\frac{\mathrm{MV}}{\sqrt{3}t_1}$ per sec., where t_1 is the time from one extreme position to the other, and a the maximum displacement. Putting $t_1=2\sqrt{3}a/\mathrm{V}$, the change of momentum per sec. $=\frac{\mathrm{MV}^2}{6a}=\frac{\alpha\theta}{3a}$.

As there are N molecules per sq. cm., the pressure within the mass is found to be $\mathrm{N}^{2/3}\frac{\alpha\theta}{3a}$ per sq. cm.

To calculate the pressure at the surface, we suppose that the molecule on the positive side of the yz plane is missing. The potential energy for a displacement x along the x-axis

$$=4f\left(l+\frac{1}{2}\frac{x^2}{l}\right)+f(l+x)$$

$$=5f(l)+xf'(l)+x^2\left\{\frac{2f'(l)}{l}+\frac{f''(l)}{2}\right\}.$$

The first term is a constant. The second gives a constant force $\mathrm{F}=f'(l)$ in the direction of the inward normal. The third term gives a force of restitution proportional to the displacement and changing sign with it. Its mean value is zero.

The permanent force, therefore, is F along the inward normal, where F is the attraction between two molecules. The pressure at the surface is $\mathrm{FN}^{2/3}$.

$$\therefore \qquad \frac{\alpha\theta}{3a}=\mathrm{F} \quad \text{or} \quad a=\frac{\alpha\theta}{3\mathrm{F}}\,.$$

This is the equation which is to replace equation (2) in the former paper.

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* A comparison of the relative magnitude of the kinetic and the potential energy terms has been given in the previous paper.

3. *Compressibility.*

To find the compressibility, we notice that the work done against the molecular forces $=\beta$ per molecule for 1° rise of temperature. Now the pressure at the surface $=\mathrm{FN}^{2/3}$. Therefore the work done against it $=3\alpha_1\mathrm{FN}^{2/3}$ where α_1 is the coefficient of linear expansion.

The work done against the inter-molecular forces per unit volume $=3\mathrm{F}\delta l\mathrm{N}=3\alpha_1\mathrm{FN}^{2/3}$, there being six molecules arranged about each individual molecule, and

$$\delta a=\delta i=\alpha_1 l.$$

$$\therefore \quad \mathrm{N}\beta=6\alpha_1\mathrm{FN}^{2/3}.$$

$$\therefore \quad \mathrm{F}=\frac{\beta}{6\alpha_1 l}, \qquad \text{since } \mathrm{N}l^3=1.$$

$$\therefore \quad a=\frac{\alpha\theta}{3\mathrm{F}}=\frac{2\alpha\theta\,.\,\alpha_1 l}{\beta}.$$

Now the surface pressure $=\mathrm{NF}^{2/3}=\dfrac{\beta\mathrm{N}}{6\alpha_1}$.

If the pressure be increased by one dyne without change of temperature, it increases by $\dfrac{6\alpha_1}{\mathrm{N}\beta}$th part of itself.

$\therefore$ a diminishes by $\dfrac{6\alpha_1}{\mathrm{NB}}$th part of itself.

$$\therefore \quad \frac{\delta a}{a}=-\frac{6\alpha_1}{\mathrm{N}\beta}=\frac{\delta l}{a}.$$

$$\frac{\delta l}{l}=-\frac{a}{l}\cdot\frac{6\alpha_1}{\mathrm{N}\beta}.$$

$$\therefore \quad \mathrm{C}=-3\frac{\delta l}{l}=\frac{18\alpha_1}{\mathrm{N}\beta}\cdot\frac{a}{l},$$

$$=36\alpha_1^2\,.\,\frac{\alpha\theta}{\mathrm{N}\beta^2}.$$

$$\therefore \quad \beta^2=36\alpha_1^2\frac{\alpha\theta}{\mathrm{CN}}$$

$$\text{or} \quad \beta=6\alpha_1\sqrt{\frac{\alpha\theta}{\mathrm{CN}}}.$$

This is the equation which has to be substituted for (4) in the former paper. It will be noticed that this value of β increases the value of F and diminishes the value of a in the ratio of 24 : 19.

4. *Face-centred Cubic Crystals.*

This arrangement consists in having a molecule placed at the eight corners of a cube and one at the centre of each of the six faces. To find the arrangement of the molecules about any individual one, we note that there are two types, viz. those at the corners and those at the centres of the faces. For both the types it will be found that the following arrangement gives the requisite number of molecules situated nearest to each individual molecule O.

With O as centre describe a sphere of radius l and draw a system of three great circles intersecting one another at right angles. Each great circle is divided into four quadrants by the other two. At the middle point of each of these twelve quadrants place a molecule. With a series of such models we can build up a body of the face-centred cubic crystal type, the edge of the cube being $\sqrt{2}l$. It may be noted that there are twelve molecules surrounding each individual molecule instead of the fourteen in the isotropic arrangement, and that the spherical distance between any two adjacent molecules not on the same co-ordinate plane is 60°. In the isotropic model the distance between any two on the same great circle is 60°.

Let us calculate the potential energy of the displacement of the central molecule. Take the planes of the great circles for the co-ordinate planes. Take two straight lines in the xy-plane, the x_1 and the y_1 axes, bisecting the angles between the x and the y axes. Place four molecules at the extremities of the x_1 and the y_1 axes. Put similarly four at the extremities of the y_2 and z_2 axes which bisect the angles between the y, z axes in the yz-plane, and also four at the extremities of the z_3 and x_3 axes which bisect the angles between the z, x axes in the zx-plane. Let (x, y, z) be the most general displacement of the central molecule. It can also be written in the form (x_1, y_1, z), (x, y_2, z_2), (x_3, y, z_3), so that

$$x^2+y^2+z^2=x_1^2+y_1^2+z^2=x^2+y_2^2+z_2^2=x_3^2+y^2+z_3^2=a^2 \quad \text{(say)}.$$

For the four molecules on the x_1, y_1 axes, the potential energy due to the displacement x_1

$$=f(l+x_1)+f(l-x_1)+2f\left(l+\frac{1}{2}\frac{x_1^2}{l}\right),$$

$$=4f(l)+x_1^2\left\{\frac{f'(l)}{l}+f''(l)\right\}.$$

That due to the displacement y_1

$$=4f(l)+y_1^2\left\{\frac{f'(l)}{l}+f''(l)\right\}.$$

That due to displacement z

$$=4f\left(l+\frac{1}{2}\frac{z^2}{l}\right),$$

$$=4f(l)+2z^2\,.\,\frac{f'(l)}{l},$$

$$=4f(l)+z^2\left\{\frac{f'(l)}{l}+f''(l)\right\}+z^2\left\{\frac{f'(l)}{l}-f''(l)\right\}.$$

The total energy due to the four molecules

$$=4f(l)+a^2\left\{\frac{f'(l)}{l}+f''(l)\right\}+z^2\left\{\frac{f'l}{l}-f''(l)\right\}.$$

The total energy due to the twelve molecules

$$=12f(l)+3a^2\left\{\frac{f'(l)}{l}+f''(l)\right\}+a^2\left\{\frac{f'(l)}{l}-f''(l)\right\},$$

$$=12f(l)+2a^2\left\{\frac{2f'(l)}{l}+f''(l)\right\}.$$

It may be noted that the variable part of the potential energy is just double of the corresponding portion of the potential energy for the cubical system. It vanishes if the force is proportional to the inverse square of the distance. This fact seems to give a special significance to the inverse-square law.

Following the same line of argument we get the following equations :—

$$a=\frac{\alpha\theta}{6\sqrt{2\mathrm{F}}},$$

$$\beta=3\left(1+\frac{1}{\sqrt{2}}\right)\alpha_1\sqrt{\frac{\alpha\theta}{\mathrm{CN}}}=5{\cdot}1\alpha_1\sqrt{\frac{\alpha\theta}{\mathrm{CN}}}.$$

This value of β is greater than the corresponding value obtained in the case of the isotropic arrangement by about 5 per cent. The value of F is increased and that of a diminished by the same amount.

June 30, 1921.

LXXXIII. *The Thermometric Anemometer.* *By* J. S. G. Thomas, *D.Sc., A.R C.Sc., A.I.C., Senior Physicist, South Metropolitan Gas Company, London*[*].

Introduction.

THE thermometric type of anemometer due to C. C. Thomas [†], which has found application in industrial practice, more especially in the measurement of large volumes of gases flowing in mains etc., is based upon the principle that if heat is imparted from a source to a stream of gas so as to raise the temperature of the stream by a constant amount, then the heat energy imparted to the gas to produce such rise of temperature is proportional to the rate of flow of the gas. Assuming constancy of the specific heat of the gas, the supply of energy to the stream to effect a given rise of temperature is independent of the initial temperature of the stream. Such a type of anemometer possesses the desirable characteristic that it measures the mass-flow of gas, and hence its indications may be made to read directly in terms of standard pressure and temperature conditions. An elaborate series of calibrations of this type of anemometer against others of the Pitot and Venturi types has been made by C. C. Thomas [‡], and over the range of velocities employed, the indications of the three types of instruments were found to be in very close agreement. The calibrations referred to were carried out in a pipe of 24 in. diameter and the lowest velocity corresponded with an hourly flow of 7,000 lb. of air, *i. e.* a mean velocity of about 230 cm. per sec. The straight lines obtained by plotting the rate of revolution of the fan producing the flow, as abscissæ against the flow determined from the indications of the Pitot, Venturi, and Electric meters respectively, were extrapolated for low values of the flow and passed through the origin of co-ordinates. Such extrapolation is justifiable in the case of the Pitot and Venturi meters. In the case of the electric meter, however, such extrapolation is clearly unjustifiable, as under no circumstances is the whole of the heat supplied to the heating coil imparted to the gas. There are necessarily heat losses due to radiation, conduction, and convection, and such losses

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[*] Communicated by the Author.

[†] Journ. Amer. Soc. Mech. Eng., xxxi. pp. 1325–1340 (1909). Journ. Franklin Inst., vol. 172, pp. 411–460 (1911). Proc. Amer. Gas Inst. vii. pp. 340–381 (1912).

[‡] See *e.g.* Journ. Franklin Inst., *loc. cit.* p. 433.

become relatively more important the less the velocity of the stream. It is clear that if the thermometers be symmetrically disposed with regard to the heating coil employed, no value of the heat supply to the latter would be such as to maintain the desired difference of temperature between the two thermometers in the absence of flow. If, however, the second thermometer be disposed closer to the heater than the first thermometer, in the absence of flow, the value of such heat supply is perfectly definite and determined principally by radiation and convection losses from the channel in which the heater is placed. The effect of the predominance of such heat losses for low velocities appears to have been overlooked in the papers already referred to *. It will be found that the curves obtained by plotting the rate of flow of gas as abscissæ against the rise of temperature due to a constant supply of energy to the heating coil as ordinates, is not asymptotic to the ordinate axis. Owing to the heat losses referred to, there exists a finite maximum temperature rise through which the stream is heated by a constant supply of energy. The value of the velocity of flow at which such maximum rise of temperature occurs is conditioned by a variety of factors, the size of pipe, heat insulation of pipe, etc. For velocities of flow less than this critical value, decreasing velocity is accompanied by a decreasing rise of temperature. Attention has been directed to the phenomenon in a previous paper †. Its consideration is of some consequence in technical practice, *e.g.*, in the design of heat interchangers or regenerator furnace-settings for the attainment of a maximum temperature in the gases to be heated.

In the technical form of thermometric meter, the ratio of maximum flow to minimum flow for correct registration is about 15 : 1, and by employing a second pair of temperature-difference resistances this ratio can be increased to about 60 : 1. Velocities quite commonly occurring in technical practice are of the order of a few cms. per sec., and upwards, and it is important to determine the forms of the calibration curves of a low capacity anemometer of the thermometric type for such velocities, and more especially the variation in such calibration curves accompanying a variation of the heat losses due to conduction and radiation. The present paper details some of the results obtained in the course of such an investigation.

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* See *e. g.* Journ. Franklin Inst., *loc. cit.* p. 447.

† Phil. Mag. vol. xli. p. 258 (1921).

Experimental.

The flow tube consisted of a brass tube of 2·011 cm. diameter wound with one layer of asbestos cord (diameter of cord about 3 mm.), inserted in the flow system as detailed in previous papers *. The supply of air was derived from a gas-holder of 5 cubic feet capacity connected with the laboratory high-pressure air service, and a steady and calculable flow of dry air in the system was established as already detailed †. The heating element employed is shown in fig. 1 (*a* and *b*). A is a portion of brass tube 6 mm. in length, exactly similar to the main flow tube. It fitted tightly within the ebonite ring B. A number of thin copper pins, bent at right angles as shown at C in fig. 1 *b*, were driven securely into holes drilled in the ebonite ring, and slots were cut of an appropriate width and depth in the brass ring A so that these pins were insulated from the latter. A length of fine platinum wire was soldered in zigzag fashion to these pins as shown, the minimum amount of solder being employed for this purpose. The ends of the wire were connected by short copper leads with the terminals T. Holes H were drilled at angular

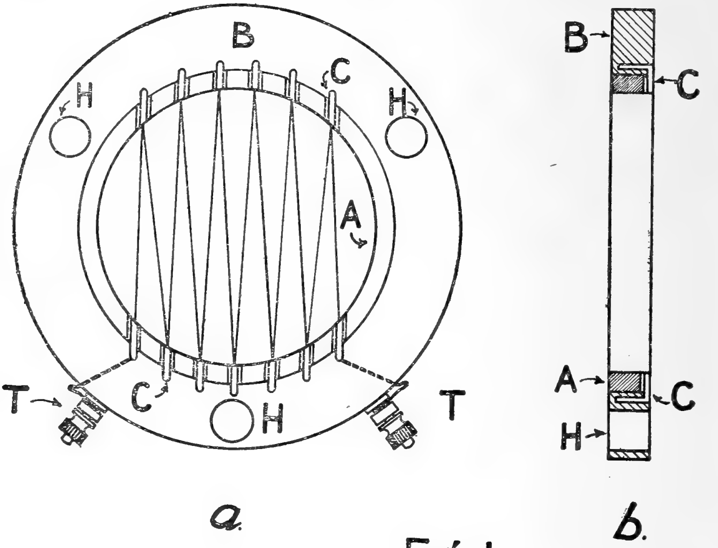

Fig. 1.

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* See *e.g.* Phil. Mag. vol. xli. p. 242 (1921).

† Phil. Mag. vol. xxxix. p. 509 (1920).

intervals of 120° C. in the ebonite ring B. These served for the insertion of the heating element in the flow system. This was effected by means of brass rods passing through the holes H and through similar holes drilled in ebonite rings attached to the main flow tube. The whole was securely fixed by means of nuts on the ends of the brass rods *. The heating element was inserted in a vertical plane in the horizontal flow system with the several wires about equally inclined to the vertical as shown in fig. 1, so that the free convection currents tended to equalize the temperature distribution across the section of the flow tube. The construction of the two platinum thermometers employed resembled that of the heating element: there was in this case, however, no necessity to employ an inner brass ring, and the pins for the support of the platinum wires were made considerably smaller than in the case of the heating element. The thermometers were inserted in the flow system in a similar manner to that employed for the insertion of the heater. The distances between the respective thermometers and the latter could be adjusted to any desired values by the use of suitable lengths of tube provided with ebonite ends affixed to the tube and suitably bored. For very small distances between heater and thermometer, thin separating disks of ebonite bored to the appropriate diameter were similarly employed. The thermometers were calibrated by the determination of their respective resistances at 0° C. and at a temperature of $50° \pm ·02°$ C., on gas scale, corresponding to $49·62 \pm 0·02°$ C. on Pt scale ($\delta = 1·5$), this temperature being maintained thermostatically in a water bath, and determined by a mercury thermometer standardized at the N. P. Laboratory. The thermometers were adjusted as nearly as possible to equality of resistance at 0° C., and they were, in use, connected differentially with a Callendar and Griffiths' bridge, the scale of which was provided with a vernier, enabling the balance to be determined to 0·01 cm. The supply of energy to the heating element was determined from a knowledge of the current supplied and the drop of potential occurring across the heater. The current was read from a Siemens & Halske ammeter reading to 0·001 amp. The voltage drop across the heater was determined by means of a Rayleigh potentiometer composed of two P O. Boxes adjusted so that their total resistance was 10,000 ohms throughout. The potentiometer readings were calibrated by means of a Weston cell standardized at the N. P. Laboratory.

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* See Phil. Mag. vol. xliii. p. 279 (1922).

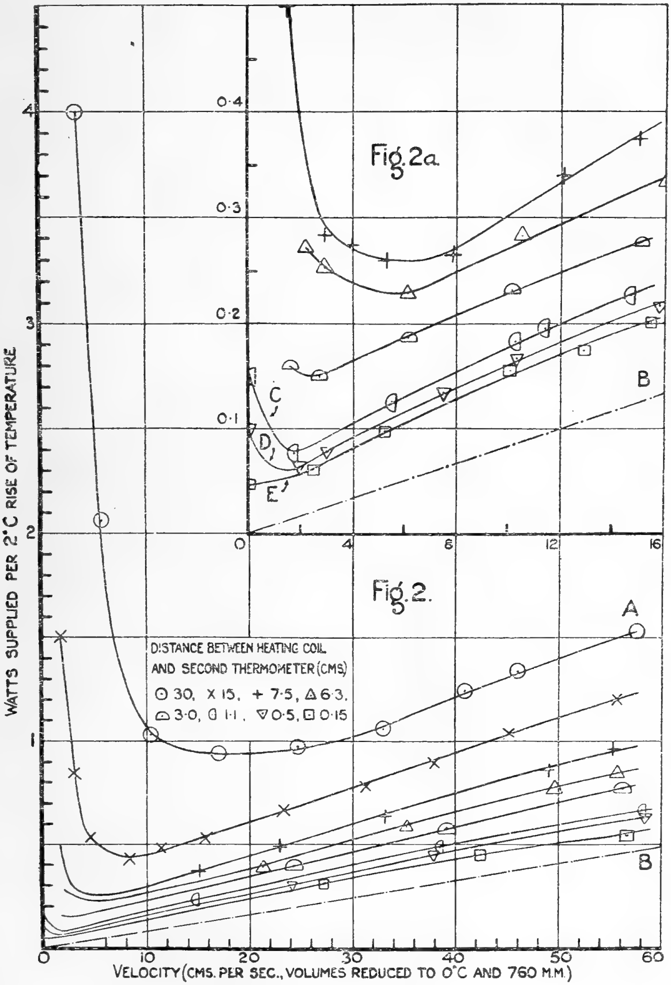
The mode of experiment was as follows :—A steady flow of dry air was established in the system for about an hour, and the balance of the Callendar & Griffiths' bridge ascertained in the absence of any current in the heating element. The point of contact on the bridge wire was then moved to the point corresponding to 2° C. difference between the two thermometers, and the value of the current in the heater adjusted until the bridge balance was restored at the point so determined. The necessary displacement at 15° C. was 2·65 cm. of bridge wire. The bridge current was throughout adjusted to 0·010 amp. On account of the relatively large thermal capacity of the flow system, a considerable time—of the order of 2 to 3 hours when the thermometers were widely separated —elapsed before the system attained a steady condition. Owing to slight inequality of the two thermometer resistances at 0° C., a slight alteration of balance accompanied a change of atmospheric temperature. Such alteration was taken account of throughout the observations. The potential drop across the heater was determined as already explained. The velocity of flow in the system was determined as detailed in previous papers.

The results were plotted in the form of curves in which the abscissæ represent velocities of flow, and ordinates the respective supplies of energy to the heater to maintain the second thermometer at a temperature 2° C. above that of the first.

Results and Discussion.

Internal diameter of flow tube	2·01 cm.
External diameter of flow tube	2·22 cm.
R_0 of 1st Thermometer (cms. of bridge wire)	363·40
Temperature coefficient of 1st Thermometer	0·003556
R_0 of 2nd Thermometer (cms. of bridge wire)	368·75
Temperature coefficient of 2nd Thermometer	0·003552
Shift of balance for 1° C. change of atmospheric temperature (cm. of bridge wire)	0·017

In fig. 2 are given the forms of the calibration curves obtained when the first thermometer was throughout placed at a distance of 30 cm. from the heating element while the distance between the latter and the second thermometer assumed the values 30, 15, 7·5, 6·3, 3·0, 1·1, 0·5, and 0·15 cm., as indicated by the respective curves. The initial portions of some of the curves are plotted on an enlarged



scale in fig. 2 *a*. The variation of distance between the heating element and the second thermometer affords a convenient method of studying the effect of a variation of the heat losses due to radiation etc. upon the form of the calibration curves. The broken line B in the figure gives the theoretical form—a straight line passing through the origin—of the calibration curve in the absence of any such losses, the whole of the energy supply being utilized to heat the air stream through 2° C. on the gas scale, In all cases within the range of velocities studied, the necessary energy supply to the heating element in order that a difference of 2° C. may be indicated by the thermometers is considerably greater than that theoretically necessary. Owing to the absence of a device for stirring the gas so as to render the temperature of the gas stream uniform over a cross section, an indication of 2° C. difference of temperature in the thermometers does not necessarily correspond exactly with a 2° C. rise of temperature of the stream. The use of any efficient stirring device was precluded by the experimental conditions in the present case and is impossible in many of the technical applications of anemometry, more especially where gas streams carrying dust etc. in suspension are to be measured.

The various calibration curves show considerable departure from the straight line B which would be obtained in the absence of any heat losses and if the temperature indicated by the second thermometer accurately represented the mean temperature of the stream. The greatest departure from the linear relation between the energy supply and the velocity is seen in the case of curve A, corresponding to the greatest distance between heating element and second thermometer, as is to be anticipated owing to the heat losses being greatest in this case.

The approximate form of the curve A can be best discussed by reference to the relation given by Callendar[*] and employed in the determination of the specific heat of gases and vapours by the continuous-flow method. Where the velocities of flow are larger than those concerned in the present series of experiments, and where the heat losses are small, Callendar has shown that $W = SQd\theta + hd\theta + \frac{k}{Q}d\theta$, where W is the energy supply to the heating element, S the specific heat of the gas, Q the mass flow, $d\theta$ the rise in temperature, $hd\theta$ the portion of heat loss independent of the flow, and $kd\theta/Q$ the residual portion of the heat loss varying inversely as the flow. Applying the appropriate value of S, and employing v the velocity of flow in place of Q, the relation becomes in the case of a flow of air in the present flow system :—$W = 0{\cdot}004147\,vd\theta + hd\theta + \frac{243{\cdot}6\,kd\theta}{v}$, representing a series of hyperbolæ, h and k being variable

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[*] See *e. g.* Phil. Trans., A. 535. p. 390 (1915).

parameters. The asymptotes are given by $v=0$ and $W=0{\cdot}004147\,vd\theta+hd\theta$. The value v corresponding to the minimum value of W is $v=242\sqrt{k}$. It is seen therefore that if the experimental conditions are such that the relation between the energy supply W and the velocity v is of the hyperbolic type discussed, corresponding to very large values of the velocity, the energy supply to maintain a difference of temperature $d\theta$ will be in excess of that represented by the curve B by an amount $hd\theta$, and practically independent of k. Moreover the thermometric type of anemometer would, under the same conditions, permit the velocity to be uniquely determined from the energy supply, only if such velocity were, in the case of the flow tube used in the present experiments, known to be either less than or greater than $242\sqrt{k}$. Similarly in the general case, when the energy supply is given in the form $W=SQd\theta+hd\theta+\frac{k}{Q}d\theta$ the minimum value of Q that can be uniquely determined from the value of the energy supply is equal to $\sqrt{\frac{k}{S}}$. The close approach to parallelism of the curve B and the various calibration curves, more particularly those for small values of the distance apart of the heating element and the second thermometer, for large values of the impressed velocity of the stream, indicates that the actual increase of temperature of the stream was very approximately 2° C. Owing to the increased facility for mixing occurring with slow flows, the same was probably true in the case of low velocities of flow also.

The calibration curve A is approximately hyperbolic. It will be noted however that for velocities of from 30 to 60 cms. per sec., the curve is slightly concave to the axis of velocities. This same feature of slight concavity is seen to be present in all the other curves of the series. This characteristic is probably attributable to the asymmetrical disposition of the resultant convection current from the heating element with regard to the two thermometers. Consider the case of curve A for which the two thermometers are disposed at equal distances of 30 cm. from the heating element. With zero flow, the two thermometers would indicate equal temperatures, and the highest temperature in the flow system would be found at the point immediately above the heating element. When a slow flow is imposed, the region of maximum temperature in the flow system is moved towards the second thermometer. The energy requisite to maintain an indicated difference of 2° C. in the two thermometers is diminished on this account below the value it would have were the region of maximum temperature not so displaced. This effect increases with increasing velocity of the stream, as with such increase of velocity, the region of maximum temperature in the flow system advances towards the second thermometer. Such increase of effect must, however, attain a limiting value as it is clear that for large values of the impressed velocity only a small proportion of the energy supplied is utilized to raise the temperature of the flow system. The form of the calibration curve A may therefore be regarded as derived from the theoretical hyperbolic form by drawing it through a series of points the ordinates of which are slightly less than those of points on the hyperbola, the proportional difference of ordinates initially increasing with increase of velocity from zero until a limiting velocity is reached, and thereafter decreasing.

The remaining calibration curves in figs. 2 and 2 *a* were obtained with the second thermometer placed closer than the first to the heating element. These curves are not asymptotic to the axis of energy supply. Clearly, with such dispositions of the respective thermometers, a finite energy supply would establish a difference in the temperatures indicated by the two thermometers. This effect is clearly seen in the curves C, D, E in fig. 2 *a*. The curve E obtained with the second thermometer placed at a distance of only 1·5 mm. from the heating element is characterized by the fact that the minimum value—if any such occur—of the energy supply necessary to maintain the indicated difference of 2° C. must correspond with a very small velocity of the stream. The lower limit of velocities of gas streams for which the thermometric anemometer may be employed is clearly reduced by reducing the distance between the heating element and the second thermometer. For low values of the velocity, the time lag of response of the thermometric anemometer to a change of velocity is conditioned principally by the distances between the heating element and the thermometers. For small time lag, these distances should be as small as possible.

The disposition of the second thermometer has been discussed above. There is also a most suitable position at which the first thermometer should be placed. Such position is clearly not at too great a distance from the heating element, nor near thereto. In the latter case the temperature indicated by it would be conditioned largely by that of the heating element and its surroundings. An indicated difference of

2° C. between the two thermometers would under these circumstances correspond to a greater rise of temperature than 2° C. in the stream. This effect is shown in fig. 3.

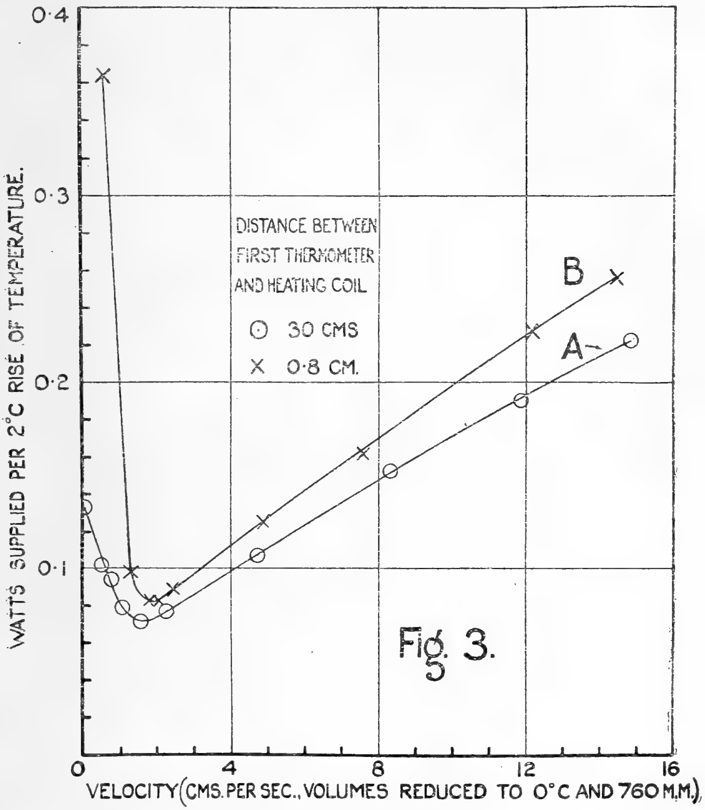

Fig. 3.

Both curves were obtained with the second thermometer at a distance of 0·8 cm. from the heating element. The respective distances of the first thermometer therefrom were 30 cm. (curve A) and 0·8 cm. (curve B).

Summary.

An experimental investigation of the application of the thermometric anemometer to the determination of slow rates of flow of gases is detailed. It is shown that values of such low velocities cannot, in general, be uniquely determined by such type of anemometer. This arises owing to the existence of a minimum value of the energy supply required to heat

the stream through a definite range of temperature. The dependence of the limiting velocity upon the disposition of the thermometers with regard to the heating element is shown by means of calibration curves obtained for various distances between the respective thermometers and heating element.

The author desires to express to Dr. Charles Carpenter, C.B.E., his thanks for the provision of the facilities necessary for carrying out the work detailed in this paper.

709 Old Kent Road, S.E.
Dec. 29, 1921.

LXXXIV. *On a Possible Physical Interpretation of Lewis and Adams' Relationship between* h, c, *and* e. *By* GERALD A. NEWGASS, *B.A.* (*Cantab.*)*.

CONSIDER the hypothetical case of two spheres carrying equal but opposite charges e, of no mass other than electromagnetic, of equal radii. Imagine that the two spheres are touching, but that they are prevented from discharging. If the system is set rotating about its centre of mass and an axis at right angles to the line joining the centres of the spheres, there will be a certain angular velocity, angular momentum, and rotational energy at which the centripetal force would balance the electrostatic attraction. These values were roughly calculated, making use of the simplifying assumptions that the electromagnetic masses as given by the equation $m=e^2/(6\pi rc^2)$ were concentrated at the centres of the spheres, and that any possible effects of relativity etc. due to the high velocities cancelled out, and it was found that while the angular velocity and the rotational energy of the system varied with the radii of the spheres, the *angular momentum was independent of the size of the system* and was given by

$$\frac{1}{2\sqrt{6\pi}}\frac{e^2}{c}.$$

If the electricity is assumed to be distributed uniformly throughout the spheres instead of on the surface, or if, instead of both spheres being equal, one is considerably larger than the other, the only effect is to alter the coefficient. Accordingly, it is suggested that if the values of the moment of inertia and angular momentum were

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* Communicated by the Author.

calculated accurately by considering each element of the field of force separately and integrating up, assuming a not improbable distribution of electricity in the spheres, the angular momentum might be found to be given by

$$16\pi^2 . \sqrt[3]{\frac{8\pi^5}{15}} . \frac{e^2}{c} .$$

This expression, if the spheres were shrunken or swollen negative or positive electrons, is that calculated by Lewis and Adams for h (Phys. Rev. (2) iii. p. 92 (1914)). And it might also be found that (2) the energy of the system was $1/c^2$ times its mass, (3) that the diameter of the system was c/ω, and (4) that the velocity of the periphery was c. In the case that has been considered the coefficients were not unity.

Regarding the physical interpretation of the critical angular velocity, there are two possibilities: (1) The radii of the spheres might be fixed; if the angular momentum were less than the critical value there would be a tendency for the spheres to fall into one another, if it were greater they would fly apart; (2) the criterion might be that the spheres were always in equilibrium, the centripetal force being equal to the electrostatic force, and this would require that the angular momentum should always have the critical value. Accordingly, it is found that the spheres would have to decrease in size with increase of energy. It is not quite clear what would cause the spheres to alter their radii in this way, but it is possible that, if there was an inward force which balanced the outward pull on the surface of the tubes of force with an increase in angular velocity, the tubes would lag behind and leave the surface of the spheres farther from the normal, and hence, the effective outward pull being reduced, the spheres would shrink. It is suggested that some such electric doublet, where the distribution was such that the coefficients were correct, is the unit of radiation.

Space free from all radiation would be considered to contain an infinite number of doublets of infinite size. If a certain volume of space is filled with homogeneous polarized radiations of frequency ω, some of these doublets would shrink and rotate with frequency ω, angular momentum h, and energy $h\omega$. If the radiation were of sufficient density, the whole volume of space would be full of rotating doublets, similar to a train of cog-wheels, the electric force at any point would be varying periodically, and there would be also a magnetic force at right angles to the plane of the rotations of the doublets also varying periodically. Each doublet would occupy a volume c/ω cube, and so would give interference effects. It is also seen that if both polarized rays are eliminated by crossed nicols no energy will get through, and it would be impossible to have "longitudinal radiation" by itself.

A source of radiation of frequency ω would consist of a number of rotating doublets. Energy would be dissipated in two ways :—(1) A doublet losing all its energy, as its periphery is moving with velocity c, would send out a pulse to infinity—if all the doublets were rotating in phase, the disruption of a number at a fairly steady rate would give the ordinary periodic radiation and interference effects ; (2) a doublet owing to a "collision" would leave the cluster and travel as a whole in a straight line from the source until through another collision it gave up all its energy—its velocity would be less than c, but would probably give effects that would appear instantaneous. Accordingly, it seems that a source could be very weak and give interference effects, and yet be able to start the photoelectric effect in an inappreciable time.

LXXXV. *On Oscillation Hysteresis in a Triode Generator with Two Degrees of Freedom.* *By* BALTH. VAN DER POL Jun., *D.Sc.*[*]

WHEN two oscillatory circuits are linked together by means of a magnetic, electrostatic, or resistance coupling, it is well known that the circuit combination possesses two degrees of freedom. If one of these oscillatory circuits is, moreover, a part of a triode generator, it is natural to ask whether the two modes of vibration can exist simultaneously or, if this is not the case, whether the one or the other mode of vibration will obtain for any particular conditions.

Now it is found experimentally that, when the system oscillates in one of the two modes of vibration and the natural frequency of the secondary circuit is varied gradually, the system suddenly jumps at a certain point from the first mode of vibration to the other. If afterwards the natural frequency of the secondary is varied in the reverse direction it is found that the system jumps from the second into the first mode of vibration, but at a point which is *not* identical with the first one mentioned above, and thus

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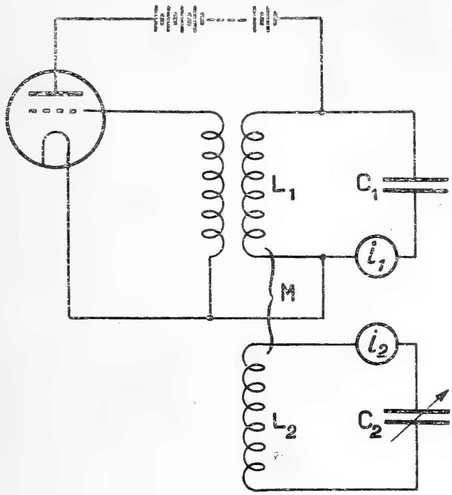
[*] Communicated by Professor H. A. Lorentz, For.M.R.S.

a kind of oscillation hysteresis is obtained, which, apart from its importance in technical applications, is of interest from a physical point of view.

The normal experimental arrangement is shown in fig. 1, where an oscillatory circuit L_2C_2 is shown coupled through

Fig. 1.



the mutual induction M to the circuit L_1C_1 belonging to a normal triode generator. We may consider the indications of the thermal ammeters i_1 and i_2 when

(i.) C_2 is brought from a small value, through the point of resonance $(L_2C_2=L_1C_1)L$, to a large value ; and

(ii.) when the value of C_2 is thereupon gradually decreased through resonance to the first small value.

The relations between i_1 and $\omega_2{}^2$ and i_2 and $\omega_2{}^2$ thus obtained are shown in figs. 2 and 3, where the arrows indicate the paths followed. Further, in these two diagrams the total system is found to vibrate for conditions represented by EFB in one of the two modes of vibration, *i. e.* with the higher one of the two coupling frequencies, while for conditions represented by DCA the system vibrates with the lower coupling frequency. Hence at the points B and A discontinuities occur in the modes of vibration, resulting in a discontinuity both in frequency and amplitudes of the currents. But, further, it is also seen from these graphs that the system has the tendency to go on oscillating as long as possible in the mode of vibration in which it is already oscillating, though the other mode of vibration is possible for the same parameters.

Fig. 2.

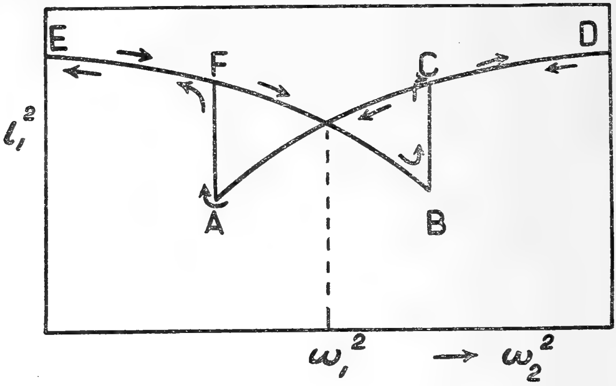
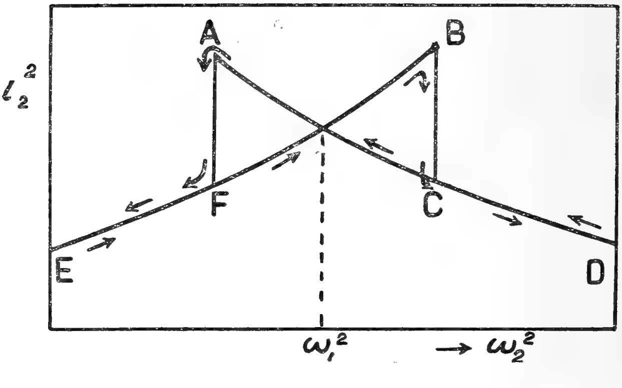


Fig. 3.



These phenomena were noticed by the author in February 1920, but it was felt that no satisfactory explanation could be given unless progress was first made in the development of a non-linear theory of sustained oscillations. For it is obvious that, when the problem is treated with linear differential equations, the principle of superposition is valid, and in this case oscillations in the one mode are uninfluenced by oscillations in the other. It is therefore somewhat surprising that up to the present, though several theoretical contributions to the problem have already appeared [*], the phenomenon has, as far as we are aware, only been dealt with in a linear theory. The solutions of the differential equations in this case are of the form $e^{\pm at} \sin \omega t$, and it depends on the sign of a whether an oscillation will build up or decay. But whether both oscillations will be present simultaneously or whether the one mode of vibration will suddenly be replaced by the other when a parameter of the circuits is gradually varied, and whether a hysteresis loop will be obtained, these questions can *not* be answered by a linear theory. In order therefore to retain in the analysis the necessary interaction of simultaneous vibrations which determines the stability of the oscillations, non-linear terms which occur through the curvature of the triode characteristics may not be ignored.

Before attempting, however, to set out a non-linear theory of the phenomena under consideration, a few remarks may first be made concerning the terminology.

The notion of one or two degrees of freedom is used here as an extension of the usual meaning attached to these terms in the ordinary linear treatment of oscillation problems. We are well aware that, *e. g.* to speak of a system as having one degree of freedom when more than one stable oscillation is possible for a given set of parameters [†] is not altogether satisfactory, but it is hoped that from the description of the phenomena the meaning will be sufficiently clear.

Further, we shall discriminate between a "possible" vibration and a vibration that can actually be realized. With "possible" is here meant a solution representing a stationary oscillation with a constant amplitude. It may, however, be that this oscillation cannot be realized, it being unstable.

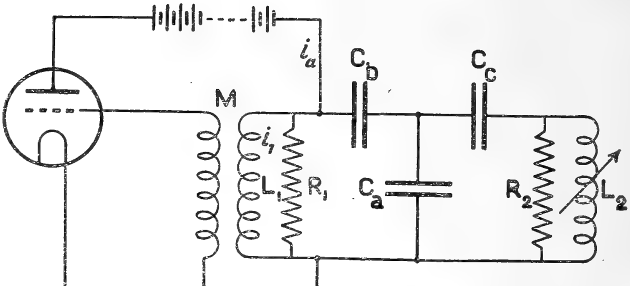
Finally, it is obvious that for a system such as shown in fig. 1, when the secondary circuit is very loosely coupled to the primary, the reaction of the secondary on the primary will be small. It is found experimentally that under these circumstances an ordinary resonance curve can be obtained as the secondary circuit. This case will, however, not be considered here and we shall confine our considerations to cases where the coupling is strong.

[*] J. S. Townsend, Radio Review, i. p. 369 (May 1920). K. Heegner, *Archiv für Elektrotechnik*, ix. p. 127 (1920). F. Harms, *Jahrbuch für drahtl. Telegraphie*, xv. p. 442 (1920). H. Vogel und M. Wien, *Ann. d. Phys.* lxii. p. 649 (1920). H. G Möller, *Jahrbuch für drahtl. Telegraphie*, xvi. p. 402 (1920). H. Pauli, *ibid.* xvii. p. 322 (1921). W. Rogowski, *Archiv für Elektrotechnik*, x. pp. 1, 15 (1921) See also Möller, *Die Elektronenröhre* (Vieweg, 1920).

[†] See, *e. g.* Appleton and Van der Pol, Phil. Mag. Jan. 1922.

In order to simplify the analysis we shall not treat the actual circuit shown in fig. 1, which, from an experimental point of view, is the simpler, but will replace the magnetic coupling by an equivalent capacity coupling. We shall also replace the series resistance of the oscillatory circuits by equivalent shunt resistances, and therefore deal with the circuit of fig. 4. In this way we retain all the essentials of the problem while, through simple phase relations, a considerable simplification of the analysis is obtained.

Fig. 4.



In fig. 4 the total equivalent capacity $\left\{\begin{matrix}C_1\\C_2\end{matrix}\right.$ of the $\left\{\begin{matrix}\text{primary}\\\text{secondary}\end{matrix}\right.$ circuit is given by

$$\frac{1}{C_1}=\frac{1}{C_a}+\frac{1}{C_b},$$

$$\frac{1}{C_2}=\frac{1}{C_a}+\frac{1}{C_c},$$

and the square of the coupling coefficient, k^2, becomes

$$k^2=\frac{C_1C_2}{C_a^{\,2}}.$$

The free angular frequency $\left\{\begin{matrix}\omega_1\\\omega_2\end{matrix}\right.$ of the $\left\{\begin{matrix}\text{primary}\\\text{secondary}\end{matrix}\right.$ circuit is further

$$\omega_1^{\,2}=\frac{1}{C_1L_1},$$

$$\omega_2^{\,2}=\frac{1}{C_2L_2}.$$

Similarly the damping coefficient $\begin{cases} \alpha_1'' \\ \alpha_2'' \end{cases}$ of the $\begin{cases} \text{primary} \\ \text{secondary} \end{cases}$ circuit is given by

$$\alpha_1''=\frac{1}{C_1R_1},$$

$$\alpha_2''=\frac{1}{C_2R_2}.$$

We call i_a the variable part of the anode current and v_a the variable part of the anode potential. The application of Kirchhoff's laws to the circuits then leads (with neglect of the grid current) to:

$$\frac{d^4v_a}{dt^4}+(\alpha_1''+\alpha_2'')\frac{d^3v_a}{dt^3}+\{\omega_1^2+\omega_2^2+(1-k^2)\alpha_1''\alpha_2''\}\frac{d^2v_a}{dt^2}$$

$$+(1-k^2)(\omega_1^2\alpha_2''+\omega_2^2\alpha_1'')\frac{dv_a}{dt}+(1-k^2)\omega_1^2\omega_2^2v_a$$

$$=-\frac{1}{C_1}\left[\frac{d^3i_a}{dt^3}+\alpha_2''(1-k^2)\frac{d^2i_a}{dt^3}+\omega_2^2(1-k^2)\frac{di_a}{dt}\right]. \quad . \quad (1)$$

We further notice that

$$v_a=L_1\frac{di_1}{dt},$$

$$v_g=-M\frac{di_1}{dt},$$

where v_g is the grid potential, so that a constant ratio exists between the variable anode potential and grid potential, namely,

$$\frac{v_g}{v_a}=-\frac{M}{L_1}.$$

Hence, though in general the anode current is a function of both the anode and grid potentials, by means of this constant ratio we are able to express the anode current as a function of the variable anode potential alone. A method of determining experimentally this relation $i_a=\psi(v_a)$ has been previously described*. For conditions for which free oscillations are possible this characteristic has in general a negative slope† for $v_a=0$. It is therefore appropriate to develop the function $i_a=\psi(v_a)$ as

$$i_a=-\alpha'v+\beta'v^2+\gamma'v^3, \quad . \quad . \quad . \quad . \quad . \quad (1\,a)$$

where the index of v_a has been dropped for simplicity as will be done in the further treatment.

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* Appleton and Van der Pol, Phil. Mag. xlii. p. 201 (1921).

† When developed in this way the theory applies equally well to "dynatron" circuits.

It may here be noticed that stable oscillations are only possible when both α' and γ' as defined by (1 a) are positive. No further terms are needed in this series to enable us to account for the hysteresis phenomenon under consideration, though, naturally, in order to obtain a more exact numerical result in all details, further terms may be necessary.

We further write

$$\begin{aligned} \frac{\alpha'}{C_1}-\alpha_1'' &= \alpha_1, \\ \alpha_2'' &= \alpha_2, \\ \frac{\beta'}{C_1} &= \beta, \\ \frac{\gamma'}{C_1} &= \gamma, \end{aligned}$$

and assume, in agreement with the usual circuit dimensions, that the initial logarithmic increment of the total primary (triode included) and the logarithmic decrement of the secondary are small compared with unity, *i. e.* that

$$0<\frac{\alpha_1}{\omega_1}\leqslant 1, \qquad 0<\frac{\alpha_2}{\omega_2}\leqslant 1.$$

On making these substitutions in (1) we arrive at

$$\begin{aligned} &\frac{d^4v}{dt^4}+(\alpha_2-\alpha_1)\frac{d^3v}{dt^3}+\{\omega_1{}^2+\omega_2{}^2-(1-k^2)\alpha_1\alpha_2\}\frac{d^2v}{dt^2} \\ &\quad +(1-k^2)(\omega_1{}^2\alpha_2-\omega_2{}^2\alpha_1)\frac{dv}{dt}+(1-k^2)\omega_1{}^2\omega_2{}^2v \\ &\quad =-\left\{\frac{d^3}{dt^3}+\alpha_2(1-k^2)\frac{d^2}{dt^2}+\omega_2{}^2(1-k^2)\frac{d}{dt}\right\}(\beta v^2+\gamma v^3). \quad . \quad . \quad . \quad (2) \end{aligned}$$

On neglecting small terms in (2) this equation can further be simplified, and we obtain as the fundamental differential equation of our problem

$$\begin{aligned} &\frac{d^4v}{dt^4}+(\omega_1{}^2+\omega_2{}^2)\frac{d^2v}{dt^2}+(1-k^2)\omega_1{}^2\omega_2{}^2v \\ &\quad +\left\{\frac{d^3}{dt^3}+\omega_2{}^2(1-k^2)\frac{d}{dt}\right\}(\beta v^2+\gamma v^3)+(\alpha_2-\alpha_1)\frac{d^3v}{dt^3} \\ &\quad +(1-k^2)(\omega_1{}^2\alpha_2-\omega_2{}^2\alpha_1)\frac{dv}{dt}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

The general solution of (3) seems not to be possible, but since we consider $\frac{\alpha_1}{\omega_1}$ and $\frac{\alpha_2}{\omega_2}$ as small compared with unity, an approximate solution can be obtained.

From the general nature of the problem two modes of vibration may be expected to be possible, and to express this mathematically we are thus led to a trial solution,

$$v = a \sin \omega_{\mathrm{I}} t + b \sin (\omega_{\mathrm{II}} t + \lambda),$$

where a and b are certain unknown functions of the time and ω_{I} and ω_{II} are unknown frequencies. λ is an arbitrary phase constant.

As

$$\frac{\alpha_1}{\omega_1} \leqslant 1, \qquad \frac{\alpha_2}{\omega_2} \leqslant 1,$$

and ω_1 and ω_2 are of the same order of magnitude, we may expect the possible building up or decay of the amplitudes to occur slowly compared with the oscillations themselves, that is,

$$\frac{da}{dt} \leqslant \omega_{\mathrm{I}} a,$$

$$\frac{db}{dt} \leqslant \omega_{\mathrm{II}} b,$$

Hence the second and higher differential coefficients of a and b with respect to time will be neglected. We thus have

$$\left.\begin{aligned}
v &= a \sin \omega_{\mathrm{I}} t + b \sin (\omega_{\mathrm{II}} t + \lambda), \\
\dot{v} &= \omega_{\mathrm{I}} a \cos \omega_{\mathrm{I}} t + \dot{a} \sin \omega_{\mathrm{I}} t + \omega_{\mathrm{II}} b \cos (\omega_{\mathrm{II}} t + \lambda) \\
&\qquad + \dot{b} \sin (\omega_{\mathrm{II}} t + \lambda), \\
\ddot{v} &= -\omega_{\mathrm{I}}^2 a \sin \omega_{\mathrm{I}} t + 2\omega_{\mathrm{I}} \dot{a} \cos \omega_{\mathrm{I}} t - \omega_{\mathrm{II}}^2 b \sin (\omega_{\mathrm{II}} t + \lambda) \\
&\qquad + 2\omega_{\mathrm{II}} \dot{b} \cos (\omega_{\mathrm{II}} t + \lambda). \\
\ddot{v} &= -\omega_{\mathrm{I}}^3 a \cos \omega_{\mathrm{I}} t - 3\omega_{\mathrm{I}}^2 \dot{a} \sin \omega_{\mathrm{I}} t - \omega_{\mathrm{II}}^3 b \cos (\omega_{\mathrm{II}} t + \lambda) \\
&\qquad - 3\omega_{\mathrm{II}}^2 \dot{b} \sin (\omega_{\mathrm{II}} t + \lambda), \\
\ddddot{v} &= \omega_{\mathrm{I}}^4 a \sin \omega_{\mathrm{I}} t - 4\omega_1^3 \dot{a} \cos \omega_{\mathrm{I}} t + \omega_{\mathrm{II}}^4 b \sin (\omega_{\mathrm{II}} t + \lambda) \\
&\qquad - 4\omega_{\mathrm{II}}^3 \dot{b} \cos (\omega_{\mathrm{II}} t + \lambda).
\end{aligned}\right\} \quad (4)$$

We shall further have to consider the terms involving v^2 and v^3. These non-linear terms obviously suggest the presence of higher harmonics and combination tones, but as the increment and decrement are small, the main effect of the non-linear terms is in their influence on the amplitudes.

For under these circumstances the series representing the amplitudes of the harmonics may be expected to converge rapidly so that the influence of the harmonics on the amplitude of the fundamental may, as a first approximation, be neglected. We are thus justified in neglecting as a first approximation the presence of these higher harmonics and combination tones and shall retain, therefore, in the terms with v^2 and v^3 only those parts involving the frequencies ω_I and ω_{II}. We thus see that the term βv^2 has no influence on the result. In considering, however,

$$v^3 = \{a \sin \omega_I t + b \sin (\omega_{II} t + \lambda)\}^3,$$

terms of several frequencies occur, such as ω_I, ω_{II}, $3\omega_I$, $3\omega_{II}$, $\omega_I + 2\omega_{II}$, $\omega_I - 2\omega_{II}$, $2\omega_I + \omega_{II}$, ... etc., but only the terms involving the frequencies ω_I and ω_{II} will be retained.

Hence we have

$$v^3 = \tfrac{3}{4}a(a^2 + 2b^2) \sin \omega_I t + \tfrac{3}{4}b(b^2 + 2a^2) \sin (\omega_{II} t + \lambda). \quad (5)$$

It may here be noticed that b occurs in the coefficient of $\sin \omega_I t$ and a in the coefficient of $\sin (\omega_{II} t + \lambda)$. This fundamental fact in the non-linear treatment of our problem shows the mutual influence of simultaneous vibrations, and it will further be found that the presence of one oscillation makes it more difficult for the other to develop. When more than three terms are used in the series expansion for i_a, as is advisable when working on the lower bottom part or higher top part of the $i_a - v_g$ characteristic, then the presence of one oscillation is, however, occasionally favourable to the development of another oscillation. Such special cases will, however, not be considered here.

We now proceed to substitute from (4) and (5) in (3) and thus get an equation of the form

$$A \sin \omega_I t + B \sin (\omega_{II} t + \lambda) + C \cos \omega_I t + D \cos (\omega_{II} t + \lambda) = 0, \quad . \; . \; . \; (5a)$$

where A, B, C, and D are functions of the variables ω_I, ω_{II}, a, b, but they also contain $\dot{a}$, $\dot{b}$, $\frac{da^3}{dt}$, $\frac{db^3}{dt}$.

These expressions A, B, C, and D contain terms of three orders of magnitude, viz.:

first order : $\omega^4 a$, $\omega^4 b$;

second order : $\alpha\omega^3 a$, $\gamma\omega^3 a^3$, $\omega^3 \dot{a}$ .... etc.;

third order : $\alpha\omega^2 \dot{a}$, $\gamma\omega^2 \frac{da^3}{dt}$ .... etc.;

but we only retain the first two orders of magnitude.

In order to satisfy (5 *a*) identically we equate separately to zero the four coefficients A, B, C, D. Thus four equations are obtained for the four variables a, b, ω_{I}, and ω_{II}. They are found to be

$$\omega_{\mathrm{I}}^4-\omega_{\mathrm{I}}^2(\omega_1^2+\omega_2^2)+(1-k^2)\omega_1^2\omega_2^2=0, \quad . \quad (6\,a)$$

$$\omega_{\mathrm{II}}^4-\omega_{\mathrm{II}}^2(\omega_1^2+\omega_2^2)+(1-k^2)\omega_1^2\omega_2^2=0, \quad . \quad (6\,b)$$

$$2(\omega_1^2+\omega_2^2-2\omega_{\mathrm{I}}^2)\frac{da}{dt}+\{(1-k^2)(\omega_1^2\alpha_2-\omega_2^2\alpha_1)$$
$$+\omega_{\mathrm{I}}^2(\alpha_1-\alpha_2)\}\,a+\tfrac{3}{4}\gamma a(a^2+2b^2)\,\{\omega_2^2(1-k^2)-\omega_{\mathrm{I}}^2\}=0, \quad . \quad . \quad . \quad (7\,a)$$

$$2(\omega_1^2+\omega_2^2-2\omega_{\mathrm{II}}^2)\frac{db}{dt}+\{(1-k^2)(\omega_1^2\alpha_2-\omega_2^2\alpha_1)$$
$$+\omega_{\mathrm{II}}^2(\alpha_1-\alpha_2)\}\,b+\tfrac{3}{4}\gamma b(b^2+2a^2)\,\{\omega_2^2(1-k^2)-\omega_{\mathrm{II}}^2\}=0. \quad . \quad . \quad . \quad (7\,b)$$

Equations (6 *a*) and (6 *b*) give us the coupling frequencies ω_{I} and ω_{II}, while (7 *a*) and (7 *b*) enable us to find the possible stationary amplitudes a and b and to determine their stability.

Since (6 *a*) and (6 *b*) are of the same form it is necessary to define ω_{I} and ω_{II} quite definitely. We shall take

$$\left.\begin{aligned}\omega_{\mathrm{I}}^2&=\tfrac{1}{2}(\omega_1^2+\omega_2^2)+\tfrac{1}{2}\sqrt{(\omega_1^2+\omega_2^2)^2-4(1-k^2)\omega_1^2\omega_2^2},\\ \omega_{\mathrm{II}}^2&=\tfrac{1}{2}(\omega_1^2+\omega_2^2)-\tfrac{1}{2}\sqrt{(\omega_1^2+\omega_2^2)^2-4(1-k^2)\omega_1^2\omega_2^2},\end{aligned}\right\} \quad (8)$$

where the roots are to be taken positive, so that

$$\omega_{\mathrm{I}}^2>\omega_{\mathrm{II}}^2,\ \omega_1^2,\ \omega_2^2,$$

and

$$\omega_{\mathrm{II}}^2<\omega_{\mathrm{I}}^2,\ \omega_1^2,\ \omega_2^2.$$

The equations (7 *a*) and (7 *b*) can further be written

$$\left.\begin{aligned}\frac{da^2}{dt}&=\mathrm{E}_{\mathrm{I}}a^2(a_0^2-a^2-2b^2),\\ \frac{db^2}{dt}&=\mathrm{E}_{\mathrm{II}}b^2(b_0^2-b^2-2a^2),\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where, with the aid of (6 *a*), (6 *b*), and (8), we have

$$\left.\begin{aligned}\mathrm{E}_{\mathrm{I}}&=\tfrac{3}{4}\gamma\frac{\omega_{\mathrm{I}}^2}{\omega_1^2}\cdot\frac{\omega_{\mathrm{I}}^2-\omega_2^2}{\omega_{\mathrm{I}}^2-\omega_{\mathrm{II}}^2},\\ \mathrm{E}_{\mathrm{II}}&=\tfrac{3}{4}\gamma\frac{\omega_{\mathrm{II}}^2}{\omega_1^2}\cdot\frac{\omega_2^2-\omega_{\mathrm{II}}^2}{\omega_{\mathrm{I}}^2-\omega_{\mathrm{II}}^2},\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and thus
$$E_I > 0,$$
$$E_{II} > 0.$$

Further, the term a_0^2 introduced in (9), represents the square of the stationary amplitude which would be obtained when an oscillation in the first mode of vibration, *i. e.* with a frequency ω_I, alone was present. Similarly b_0 is the stationary amplitude which would be attained if the system vibrated only in the second mode of vibration. These amplitudes a_0^2 and b_0^2 are obtained directly from (7 *a*) and (7 *b*) by putting $\frac{da}{dt} = \frac{db}{dt} = 0$ and are found to be

$$\left.\begin{aligned} a_0^2 &= \frac{\alpha_1}{\frac{3}{4}\gamma} - \frac{\omega_I^2 - \omega_1^2}{\omega_I^2 - \omega_2^2} \cdot \frac{\omega_1^2}{\omega_2^2} \cdot \frac{\alpha_2}{\frac{3}{4}\gamma}, \\ b_0^2 &= \frac{\alpha_1}{\frac{3}{4}\gamma} - \frac{\omega_1^2 - \omega_{II}^2}{\omega_2^2 - \omega_{II}^2} \cdot \frac{\omega_1^2}{\omega_2^2} \cdot \frac{\alpha_2}{\frac{3}{4}\gamma}. \end{aligned}\right\} \quad . \quad . \quad . \quad (9\,a)$$

However, a_0 and b_0 are not the only "possible" stationary amplitudes as may be seen from (9) by putting

$$\frac{da^2}{dt} = 0, \quad \frac{db^2}{dt} = 0.$$

We thus have in general for the "possible" stationary amplitudes a_s and b_s the two equations

$$a_s^2(a_0^2 - a_s^2 - 2b_s^2) = 0,$$
$$b_s^2(b_0^2 - b_s^2 - 2a_s^2) = 0,$$

the four sets of solutions of which are

$$\left.\begin{array}{lll} \text{(i.)} & a_s^2 = 0, & b_s^2 = 0, \\ \text{(ii.)} & a_s^2 = \frac{1}{3}(2b_0^2 - a_0^2), & b_s^2 = \frac{1}{3}(2a_0^2 - b_0^2), \\ \text{(iii.)} & a_s^2 = a_0^2, & b_s^2 = 0, \\ \text{(iv.)} & a_s^2 = 0, & b_s^2 = b_0^2. \end{array}\right\} \quad (11)$$

But we shall further have to investigate separately which one of these four stationary solutions (11) will be attained in any given circumstances. Therefore (9) would have to be solved, which is a difficult, if not impossible, matter. However, in order to investigate the *stability* of each of the four solutions (11) we may consider the effect of a small forced change of amplitude from the stationary value due to some disturbing cause, and investigate the tendency of the amplitude either to return to or to depart further from its initial stationary value, thus applying the usual method in questions of dynamic stability. In this way we shall find a certain conservatism of the system in that the particular mode of vibration persists (when one parameter is varied gradually) even when conditions have been reached which are not favourable to it and which are such that, were this mode of vibration not actually present, yet the other one would exist. In other words, *metastable* oscillation conditions may arise.

Let these small changes of amplitude be represented by the type δ. We thus substitute in (9)

$$a^2 = a_s^2 + \delta a_s^2,$$
$$b^2 = b_s^2 + \delta b_s^2,$$

and only retain first powers of the small quantities δa_s^2 and δb_s^2. Hence we have

$$\left.\begin{aligned} \frac{d(\delta a_s^2)}{dt} &= \mathrm{E_I}(a_0^2 - 2a_s^2 - 2b_s^2)\delta a_s^2 - 2\mathrm{E_I} a_s^2 \delta b_s^2, \\ \frac{d(\delta b_s^2)}{dt} &= \mathrm{E_{II}}(b_0^2 - 2b_s^2 - 2a_s^2)\delta b_s^2 - 2\mathrm{E_{II}} b_s^2 \delta a_s^2. \end{aligned}\right\} \quad (12)$$

These linear equations (12) are solved by putting

$$\delta a_s^2 = \mathrm{A}' e^{kt},$$
$$\delta b_s^2 = \mathrm{B}' e^{kt},$$

and we obtain as characteristic equation for k

$$\begin{aligned} k^2 + k\,\{\mathrm{E_I}(2a_s^2 + 2b_s^2 - a_0^2) + \mathrm{E_{II}}(2a_s^2 + 2b_s^2 - b_0^2)\} \\ + \mathrm{E_I E_{II}}\,\{(2a_s^2 + 2b_s^2 - a_0^2)(2a_s^2 + 2b_s^2 - b_0^2) - 4a_s^2 b_s^2\} = 0. \end{aligned} \quad . \;. \;. \;. \quad (13)$$

In order that a set of stationary values a_s and b_s should be stable neither of the two roots k of (13) may be positive as this would show the tendency of the system to depart from the stationary solution in question.

A set of stationary amplitudes a_s and b_s is therefore only stable when

$$\left.\begin{aligned} &\mathrm{E_I}(2a_s^2 + 2b_s^2 - a_0^2) + \mathrm{E_{II}}(2a_s^2 + 2b_s^2 - b_0^2) > 0 \\ \text{and}\quad &(2a_s^2 + 2b_s^2 - a_0^2)(2a_s^2 + 2b_s^2 - b_0^2) - 4a_s^2 b_s^2 > 0. \end{aligned}\right\} \quad (14)$$

We shall now proceed to investigate the conditions of stability of our four solutions i., ii., iii., iv. of (11) separately.

i. $a_s^2=0, \qquad b_s^2=0.$

After substitution of these values in (14) we find as the condition for which both amplitudes remain zero:

$$-a_0^2\mathrm{E}_{\mathrm{I}}-b_0^2\mathrm{E}_{\mathrm{II}}>0$$

and $$a_0^2b_0^2>0,$$

or, as E_{I} and E_{II} are both positive,

$$a_0^2<0$$

and $$b_0^2<0.$$

These inequalities are expressions for the fact that *only* when the circuit conditions (resistances, retroaction, etc.) are such that no oscillations are "possible" at all, can the system be kept in the non-oscillatory state, from which it may be concluded that, when oscillations *are* "possible" at all, some form of oscillation (either ii., iii., or iv.) will build up automatically.

ii. $$a_s^2=\tfrac{1}{3}(2b_0^2-a_0^2),$$
$$b_s^2=\tfrac{1}{3}(2a_0^2-b_0^2).$$

This represents the case in which *both* coupling frequencies would be present simultaneously. But the conditions of stability here are from (14) easily found to be

$$\left.\begin{aligned}\mathrm{E}_{\mathrm{I}}a_s^2+\mathrm{E}_{\mathrm{II}}b_s^2>0\\ -a_s^2b_s^2>0.\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (15\,a,b)$$

Now for a_s and b_s to be possible at all we must obviously have

$$a_s^2>0$$

$$b_s^2>0,$$

which relations are incompatible with (15 *b*). We thus see that the simultaneous occurrence of finite stationary oscillations of both the coupling frequencies represents an unstable condition and can therefore not be realized in practice.

This is in complete agreement with the experimental results.

We saw (i.) that when a vibration is possible at all the system will automatically start vibrating in some form. It cannot, however, produce stationary oscillations in both frequencies at the same time (ii.), so that only one of the two coupling frequencies will build up. Which one this will be depends on the circumstances and can be found from a consideration of

iii. $a_s^2 = a_0^2, \quad b_s^2 = 0,$

iv. $a_s^2 = 0, \quad b_s^2 = b_0^2.$

These cases may be conveniently treated together. Before considering, however, in detail the stability of the system when oscillating in *one* mode of vibration only, we shall first determine the conditions for which such an oscillation is "possible" at all, apart from its stability. Moreover, as the peculiar discontinuities, described in the introduction, occur when the natural frequency of the secondary circuit is altered, we shall leave all parameters unaltered except the detuning of the secondary and consider how these possible amplitudes a_0 and b_0 vary as a function of this detuning. For the circuit under consideration this variation of ω_2 is brought about by varying L_2 (fig. 4), which is equivalent to a variation of the secondary capacity in a case where the electrostatic coupling here considered is replaced by its electromagnetic equivalent.

Now (9 *a*) can be written

$$\left.\begin{aligned} \tfrac{3}{4}\gamma\frac{a_0^2}{\alpha_2} &= \frac{\alpha_1}{\alpha_2} - f_{\mathrm{I}}(\omega_2^2), \\ \tfrac{3}{4}\gamma\frac{b_0^2}{\alpha_2} &= \frac{\alpha_1}{\alpha_2} - f_{\mathrm{II}}(\omega_2^2), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (16)$$

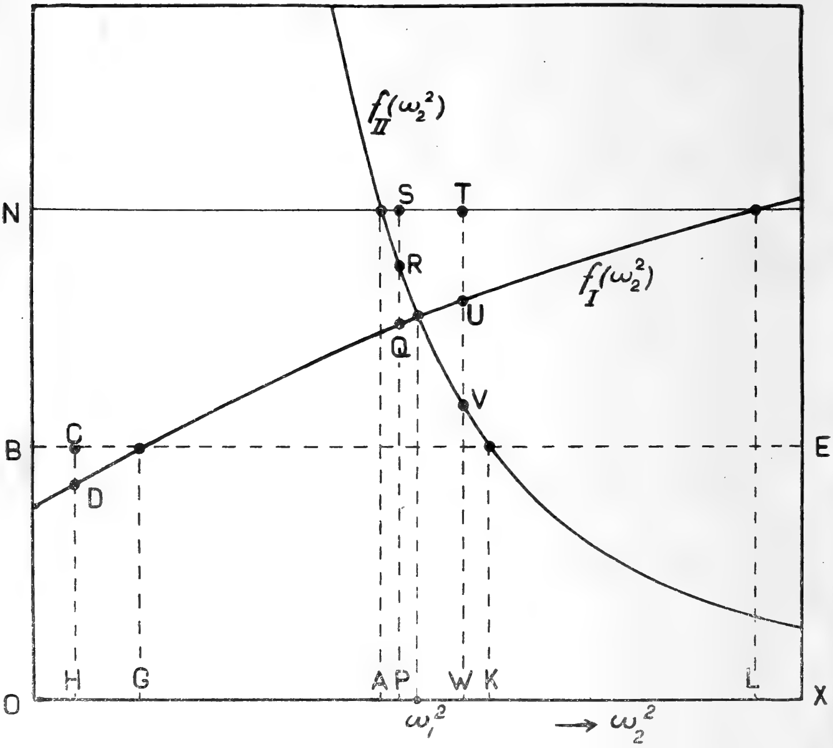
where

$$\left.\begin{aligned} f_{\mathrm{I}}(\omega_2^2) &= \frac{\omega_{\mathrm{I}}^2 - \omega_1^2}{\omega_{\mathrm{I}}^2 - \omega_2^2} \cdot \frac{\omega_1^2}{\omega_2^2} \\ \text{and} \qquad f_{\mathrm{II}}(\omega_2^2) &= \frac{\omega_1^2 - \omega_{\mathrm{II}}^2}{\omega_2^2 - \omega_{\mathrm{II}}^2} \cdot \frac{\omega_1^2}{\omega_2^2} . \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (17)$$

These functions f_{I} and f_{II} are the coefficients with which the damping coefficient of the secondary must be multiplied in order to transpose the secondary damping to the primary circuits. They are represented in fig. 5 for a constant $k^2=0\cdot5$. Since in (16) α_1, α_2 and γ are independent of ω_2 we can trace in the latter diagram the dependence of a_0^2 and b_0^2 on $\frac{\alpha_1}{\alpha_2}$ and ω_2^2.

For example, if $\frac{\alpha_1}{\alpha_2}$ is represented by OB the amplitude a_0^2 is by (16) proportional to the vertical distance between the

Fig. 5.



line BE and the curve $f_{\text{I}}(\omega_2^2)$. In a similar way b_0^2 is proportional to the distance between BE and $f_{\text{II}}(\omega_2^2)$. Thus when $\omega_2^2=\text{OH} < \text{OG}$, a_0^2 is proportional to CD, but when $\omega_2^2 > \text{OG}$, a_0^2 would be negative and oscillations of the frequency ω_{I} are impossible. In the same way oscillations of the frequency ω_{II} are only possible when $\omega_2^2 > \text{OK}$.

If we next consider a larger value of $\frac{\alpha_1}{\alpha_2}$, *e.g.* $\frac{\alpha_1}{\alpha_2}=\text{ON}$, markedly different possibilities arise. For example, the range of values of ω_2^2 for which a_0^2 is possible is now represented by OL and is seen to extend *beyond* the resonance position $\omega_2^2=\omega_1^2$. In the same way the amplitude b_0^2 is now possible for all values of ω_2^2 greater than OA. Hence a region AL for ω_2^2 exists in which both modes of vibration are separately "possible." We thus must have recourse to a consideration of the conditions of *stability* in order to decide which mode of vibration will actually be present for any given conditions.

Now in order that

$$a_s^2=a_0^2, \quad b_s^2=0 \quad \text{be stable,}$$

we must have according to (14)

$$\left.\begin{aligned} \mathrm{E_I}a_0^2+\mathrm{E_{II}}(2a_0^2-b_0^2) &> 0 \\ \text{and} \qquad a_0^2(2a_0^2-b_0^2) &> 0, \end{aligned}\right\} \quad . \quad . \quad . \quad (18\,a,\,b)$$

where the second condition is the more stringent one.

Hence for a_0^2 only to be stable, we must have

$$a_0^2 > \tfrac{1}{2}b_0^2,$$

and similarly for b_0^2 only to be stable we must have

$$b_0^2 > \tfrac{1}{2}a_0^2.$$

These conditions are represented in fig. 5 for $\frac{\alpha_1}{\alpha_2}=\mathrm{ON}$. The vertical SP is so chosen that SR=RQ and the vertical TW such that TU=UV. Hence, though we found previously AL as the region where a_0^2 as well as b_0^2 were separately "*possible*", we may now further conclude that the common region where a_0^2 as well as b_0^2 are separately *stable* is given by the smaller distance PW only.

Which one of the two possible and stable oscillations $a_0 \sin \omega_{\mathrm{I}}t$ or $b_0 \sin(\omega_{\mathrm{II}}t+\lambda)$ will be attained in the region PW? The answer to this question, which must also include the explanation of the hysteresis effect, is given by (9), and will be seen to depend on the initial conditions. For let us see what happens when ω_2^2 is gradually brought from a small value such as represented by OH, through resonance to a big value represented by OX. (We again assume $\frac{\alpha_1}{\alpha_2}$ to be given by ON.)

First, when $\omega_2^2=\mathrm{OH}$, only the first mode of vibration is possible and stable and we therefore have

$$a_s^2=a_0^2, \quad b_s^2=0.$$

Whether b^2 has the tendency to build up when once $a_s^2=a_0^2$ and $b^2=0$, is seen from (9 *b*), which can be written

$$\frac{d\log b^2}{dt}=\mathrm{E}_{\mathrm{II}}(b_0^2-2a_0^2),$$

which shows that $\log b^2$ or b^2 itself will only increase when ω_2^2 has been given such a value that

$$b_0^2-2a_0^2>0.$$

This is the case when

$$\omega_2^2=\mathrm{OW} \quad (\text{fig. } 5).$$

We can therefore bring ω_2^2 from a value $\omega_2^2<\omega_1^2$ through resonance ($\omega_2^2=\omega_1^2$) to a value $\omega_2^2=\mathrm{OW}>\omega_1^2$ while all the time the system continues to vibrate in the first mode only. But as soon as ω_2^2 has reached the value OW where the square of the amplitude which would obtain if the system vibrated in the second mode only equals twice the square of the amplitude of the vibrations in the first mode actually present ($b_0^2=2a_0^2$ or TV=2TU), then the oscillation suddenly jumps from the first mode to the second. A further increase of ω_2^2 to any bigger value will leave the second mode only present. In the same way bringing ω_2^2 back from a big value through resonance to a smaller value results in the second mode being present up to the point P where $2b_0^2=a_0^2$. It is therefore clear that the mode of vibration once obtained persists up to the point where it is no longer *stable* (*not*, as occasionally stated in a linear treatment, where it is no longer *possible*) though a region may have been traversed where the other mode would separately be stable, and thus the hysteresis effect found experimentally can be explained by theory.

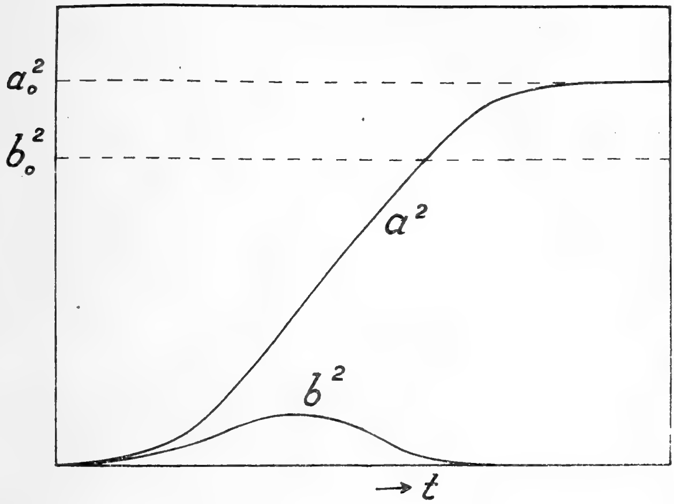
Another experimental fact can further be found theoretically. When one branch of the primary circuit, such *e. g.* as the grid circuit, is first open and thereupon the circuit is closed, then it is found that in general when $\omega_2^2<\omega_1^2$ only vibrations of frequency ω_{I} build up, while, when $\omega_2^2>\omega_1^2$, the system starts vibrating in the second mode.

The initial conditions here are therefore

$$\text{for} \quad t=0, \quad a^2=b^2=0.$$

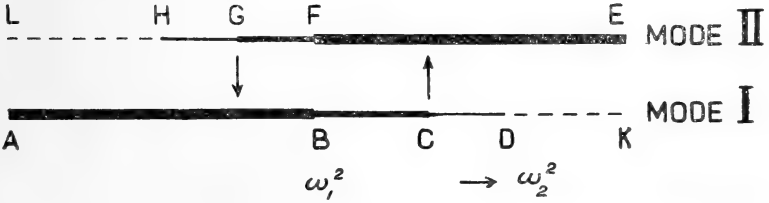
Now (9) may be integrated graphically for these initial conditions, and fig. 6 is the result for a special case where $\omega_2^2<\omega_1^2$ and therefore $a_0^2>b_0^2$. This figure shows clearly how originally both vibrations build up simultaneously but also that the initial rate of increase of b^2 is smaller than that of a^2. Further, as follows directly from (9), b^2 reaches its maximum when $b^2 = b_0^2 - 2a^2$, and thereupon it goes back asymptotically to zero while a^2 increases up to a_0^2, its stationary value.

Fig. 6.



Summing up, our results can be described in short with the aid of the schematic fig. 7. Mode I. is *stable* for $\omega_2^2 < \omega_1^2$ (AB), Mode II. for $\omega_2^2 > \omega_1^2$ (EF). Mode I. is *metastable* for $\omega_2^2 > \omega_1^2$ but only up to the point C (BC); Mode II. is metastable for $\omega_2^2 > \omega_1^2$ up to the point G (FG). The part CD is *unstable* for Mode I., and the part GH for Mode II. DK represents the part where Mode I. is

Fig. 7.



impossible at all, LH the impossible part for Mode II. On closing the primary circuit only stable oscillations are obtained, while the metastable states can only be realized when the system is first in a stable state and thereupon slowly (compared with the damping coefficients) (or adiabatically) brought to the metastable state.

Some doubt, however, still exists whether it is exactly the point of resonance which separates the regions where on closing the primary circuit either a_0^2 or b_0^2 is finally attained, as some dissymmetry still exists in the formulæ ($E_{II} \neq E_I$).

But a value for ω_2^2 very close to ω_1^2 may easily be obtained experimentally for which it is a mere matter of chance whether a_0 or b_0 will finally be obtained. A simple way of demonstrating this fact is by putting a big leaky condenser in series with the grid of the triode circuit. It is well known that with this arrangement the oscillations are periodically quenched in an automatic way, so that regular trains of vibrations are obtained. The group frequency may *e. g.* be made of the order of one second. When next the secondary circuit is coupled to the primary we can, with a heterodyne arrangement, produce an audible combination tone corresponding to either the one or the other of the two frequencies ω_I and ω_{II}. In general, each time only one of these two combination tones is obtained, but with ω_2 close to or equal to ω_1, the combination tone heard every second jumps erratically between the two tones corresponding to ω_I and ω_{II} respectively, and it is a mere matter of chance which one of the two occurs.

Finally, (9 *a*) yields for $\omega_1=\omega_2$

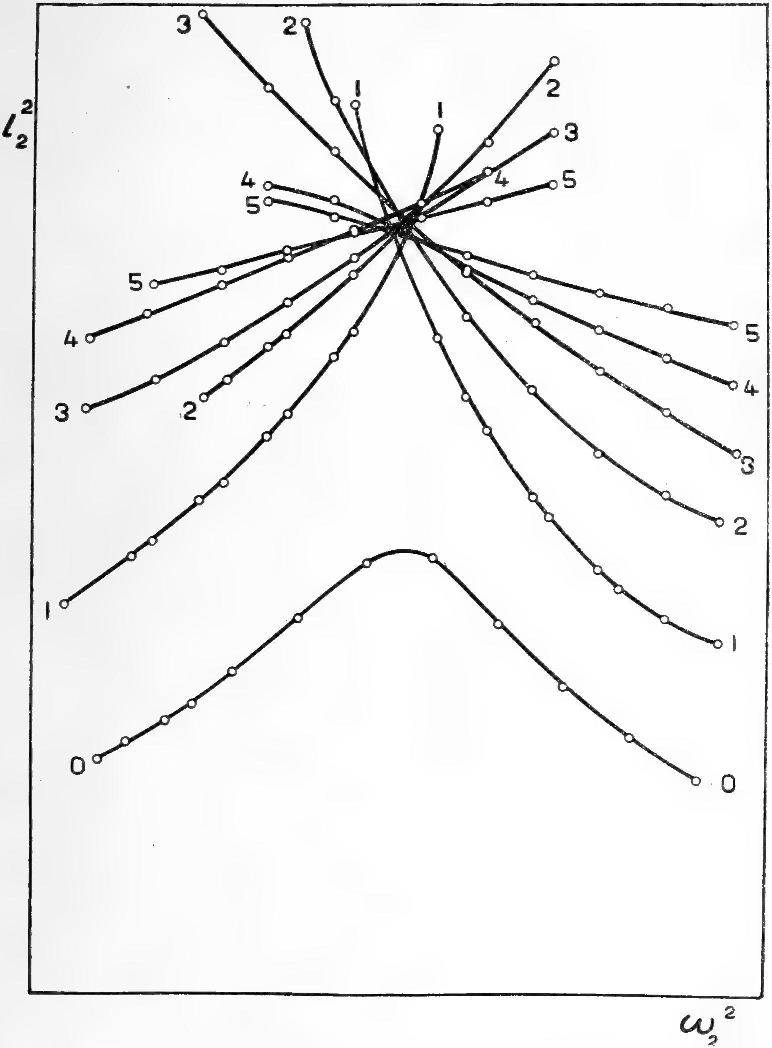
$$a_0^2=\frac{1}{\frac{3}{4}\gamma}(\alpha_1-\alpha_2),$$

$$b_0^2=\frac{1}{\frac{3}{4}\gamma}(\alpha_1-\alpha_2),$$

and thus shows that, as far as our approximations go, the two amplitude curves intersect at the point of resonance. But, moreover, these amplitudes at the resonance point are independent of the coupling coefficient. Fig. 8, which gives a set of observations of the mean square secondary current (in a circuit like that of fig 1) as a function of ω_2^2 for different coupling coefficients (increasing with the numbers 0, 1, 2, 3, 4, 5), is a confirmation of this theoretical result. For very loose coupling (Curve 0) an ordinary resonance curve is obtained, but for closer coupling (1, 2, 3, 4, 5) the figure clearly shows that the intersection of the two branches

(1—1), (2—2), etc., occurs practically at resonance and for all curves at the same height.

Fig. 8.



In conclusion my sincere thanks are due to Professor H. A. Lorentz for his kind interest and some valuable suggestions.

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LXXXVI. *Polarization Phenomena in X-ray Bulbs.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

MR. S. RATNER in the January issue of the Philosophical Magazine contributed a paper, entitled "Polarization Phenomena in X-ray Bulbs," in which he describes certain experiments made with vacuum tubes, and puts forward certain explanations.

Mr. Ratner, however, appears to have overlooked some previous contributions which have an important bearing on the subject of his investigation, and which in fact would seem to anticipate some of his results and contradict some of his conclusions.

I refer particularly to the publications of Winkleman in 1901, of Campbell Swinton later, and my own notes in the Proceedings of the Cambridge Philosophical Society, vols. xvi. and xvii. of 1912.

The results of these investigators challenge Mr. Ratner's opening statement that "Hitherto the sparking potential in well exhausted vacuum tubes has been considered to be the property of the gas in the tube, being determined entirely by the nature and the pressure of the gas."

It is well known that the disposition of the electrodes within the evacuated envelope exercises a profound effect; one only has to mention the Lodge rectifying valve in this connexion to illustrate the point.

In the notes above cited it was pointed out that a probable explanation of the influence of the position of the electrodes on the hardness of the vacuum tube was to be sought in the charge gathering on the walls of the tube surrounding the cathode, and some supporting experimental evidence was adduced.

Such an effect would clearly be influenced by the amount of metal sputtered on the walls during the working of the tube. In fact, many if not all peculiarities in working such tubes which I have so far met, receive at any rate qualitative explanation on the lines just mentioned.

Yours faithfully,
R. WHIDDINGTON.

The University, Leeds,
January 28, 1922.

LXXXVII. *Application of the Electron Theory of Chemistry to Solids.* *By* Sir J. J. Thomson, *O.M.*, *F.R.S.**

IN discussions on the structure of solids and crystals attention is usually confined to the distribution of the atoms and little or no consideration given to that of the electrons. On the view I discussed in the Phil. Mag. Mar. 1921 the electrons play a very important part in determining the arrangement of the atoms and the properties of the substance.

Each kind of atom has associated with it a definite number of electrons which form its outer layer when it is in a free state: it is by the rearrangement of these electrons that it is able to hold other atoms, whether of the same or different kinds, in chemical combination. When these atoms aggregate and form a solid there will be in each unit volume of the solid a definite number of these electrons, and the problem is to distribute the electrons so that they will form with the atoms a system in stable equilibrium.

We shall begin with the simplest case when the atoms are all of the same kind, *i. e.* when the solid contains only one chemical element. We suppose that the electrons are arranged as a series of cells which fill space and that each cell surrounds an atom; the number of cells is equal to the number of atoms. If the atom is monovalent the number of electrons is equal to the number of atoms, if divalent to twice that number, if trivalent to thrice that number, and so on. This condition will determine the shape of the cell. If the cells have to be similar and equal and to fill up space without leaving gaps, they must be of a limited number of types. These are as follows:—

(1) Parallelepipeda: if the atoms are of the same kind these may be expected to be cubes. (2) Hexagonal Prisms. (3) Rhombic Dodecahedra. (4) Cubo-octahedra.

Let us consider these in order.

Parallelepipeda.

If there is an electron at each of the eight corners of the parallelepipedon, then since each corner is common to eight parallelepipeda, the number of electrons is equal to the number of cells. Thus this is a possible arrangement for monovalent elements. If all the atoms are of the same kind the parallelepipeda will be cubes and the atoms themselves will be on the simple space lattice formed by their centres.

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* Communicated by the Author.

If electrons are placed at the centres of each of the six faces of the cubes as well as at the corners, since each middle point is shared by two cubes, each of the six central electrons will count as one half; the number of electrons will be four times the number of cells, so that this is a possible distribution for a tetravalent element.

The atoms at the centres of these cells may either form a rectangular space lattice of the simplest kind, or a system built up of different lattices; since a series of layers of these face-centred cubes will still fit, if one layer, for example, a horizontal one, is moved relatively to the layer above or below it parallel to a diagonal of a horizontal face of the cube and through a distance equal to one-half the length of the diagonal. By moving the layers about in this way we can get distributions of the atoms corresponding to the distributions of the centres of the spheres in the different methods of piling shot.

If instead of placing electrons at the centres of the faces we place them at the middle points of the twelve edges of the cube, since each middle point is shared by four cubes, these twelve electrons count as three, so that in this arrangement, as in the previous one, the number of electrons will be four times the number of cells. This arrangement would be possible for a tetravalent element; we shall see, however, that it is much less stable than the previous one.

Another symmetrical arrangement with cubical cells is one where four electrons at the corners of a regular tetrahedron are placed inside the cell. These are to be placed according to the following plan:—Let AB be two points at the opposite ends of a diagonal of one of the faces of the cube, C and D the ends of the diagonal of the parallel face, CD being at right angles to AB. Join O, the centre of the cube, with ABCD; measure from O equal lengths, OP, OQ, OR, OS, along OA, OB, OC, OD; then P, Q, R, S will be the corners of a tetrahedron symmetrical with respect to the cube. If there are electrons at each corner of the cube this arrangement will give five electrons per cell.

The preceding arrangements are all symmetrical with respect to three axes at right angles to each other and so would correspond to the cubical system in crystallography.

If instead of placing electrons at the centres of all the faces of the cubes we place them only on the faces at right angles to the axis of x, we get a distribution which gives two electrons per cell but which is not symmetrical about the three axes x, y, z, and so could not correspond to a crystal belonging to the cubical system, but to one belonging to some uniaxial system. If we put electrons at the centres of the faces at right angles to y as well as those at right angles to x, we get a system with three electrons per cell and again having a uniaxial symmetry.

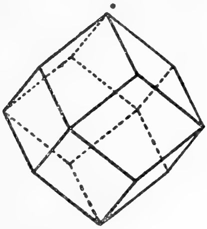
Hexagonal Prisms.

When the electrons are at the corners of a hexagonal prism, since each corner is the meeting place of six prisms, the twelve electrons at the corners of the prism will give an average of two electrons per cell. This would be a suitable arrangement for a divalent element. The arrangement of electrons would have a symmetry corresponding to that of the hexagonal system in crystallography. If, in addition, we place electrons at the middle points of the flat ends of the prism, each of these points will be shared by two prisms; this arrangement will give an extra electron per cell, so that there will be on the average three electrons per cell, a possible arrangement for a trivalent element.

If electrons are placed at the middle points of the six side faces there will be three more electrons per cell, so that each cell will account for five electrons if there are no electrons at the flat ends and for six if there are, and would give arrangements suitable for pentavalent and hexavalent elements.

The atoms accompanying the electrons will also be arranged in hexagonal prisms; each of these prisms will have an atom at the centre of each end.

Fig. 1.



The Rhombic Dodecahedron. (Fig. 1.)

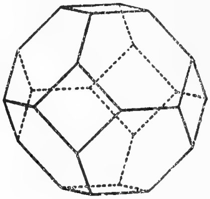
There are six corners at which four edges meet and eight at which only three meet; when the dodecahedra are fitted together so as to fill space each of the four edged corners is the meeting-place of six dodecahedra, and each of the three edged corners of four; thus there will, on the average, be three electrons to each of these cells. This would correspond to a trivalent element and would possess cubical symmetry. The disposition of the *atoms* round the dodecahedron is as follows :—

Let us call the corners where four edges meet the octahedral points, as these points are at the corners of a regular octahedron, and let us take the axes of the octahedron as the axes of x, y, and z. Each of these octahedral points, *e. g.* P the one whose coordinates are $(0, 0, d)$, has four atoms round it, in a plane through P at right angles to the line joining the point P to the centre O; the lines joining P to these atoms are parallel to the two axes of the octahedron which are at right angles to OP, and the distance of each of these atoms from P is equal to d the distance of P from the centre. In addition to these atoms there is one at the centre of each dodecahedron. It will be seen that this arrangement of the atoms is equivalent to that of a system of face-centred cubes, the centres of the cubes being at the octahedral points of the dodecahedra and the sides of the cubes parallel to the octahedral axes.

The Cubo-octahedron.

This has twenty-four corners, and when the cells are packed together so as to fill space each of the corners forms a part of four cells ; there will be thus on the average six electrons to each cell, so that this gives a symmetrical arrangement for the arrangement of the electrons in a hexavalent solid. (Fig. 2.)

Fig. 2.



The disposition of the atoms may be represented as follows :—Take the centre of one of the cells as origin and the perpendiculars to the three square faces as the axes of coordinates, then the atoms are represented by two lattices ; in (1) the coordinates of a point on the lattice are represented by pd, qd, rd, where p, q, r are *even* positive *or* negative integers and d is the distance of one of the plane faces from the centre of the cell ; in (2) the coordinates are represented by *pd*, *qd*, *rd*, where *p*, *q*, *r* are positive or negative integers, two of these must be odd and one even. These two lattices are again equivalent to a system of face-centred cubes.

The preceding results may be summed up in the following table, where the first column gives the valency of the atom, the second the possible shapes of the cells formed by its electrons, and the third the nature of the symmetry of the arrangement.

Valency.	*Shape of Cell.*	*Symmetry.*
1.	Cube with electrons at the corners	cubical.
2.	Hexagonal prisms	hexagonal.
	Cubes with electrons at the centres of one set of parallel faces	tetragonal.
3.	Hexagonal prisms with an electron at the centre of each end	hexagonal.
	Cubes with electrons at the centres of two sets of parallel faces	tetragonal.
	Rhombic dodecahedron	cubical.
4.	Face-centred cube	cubical.
	Hexagonal prism with two electrons along the axis at equal distances from the centre	hexagonal.
5.	Hexagonal prisms with electrons at the centres of the side faces	hexagonal.
	Electrons at the corners of cubes with a regular tetrahedron of electrons inside	cubical.
6.	Hexagonal prisms with electrons at the centres of all faces	hexagon.
	Cubo-octahedron	cubical.
	Face-centred cube with two electrons inside	tetragonal.
7.	Electrons at the corners of a cube with six electrons inside at the corners of a regular hexahedron	cubical.
	Electrons at the corners and centres of side faces of a hexagonal prism with two electrons inside, on the axis, at equal distances from the centre	hexagonal.

Though the table is not complete it will be seen that for most of the valencies more than one arrangement of the electrons is possible, indicating that for such elements there might be allotropic modifications with different crystalline forms.

Hitherto we have supposed that the cells in which the electrons may be arranged are regular solids, that the parallelepipeda are cubes, the hexagonal prisms regular, and so on; it is evident, however, that such an assemblage of regular cells with the atoms at their centres will, if it be strained homogeneously in any way without fracture, still remain an assemblage of cells which would enclose an atom in each cell and have the right number of electrons per cell. Thus the cubes might be distorted into parallelepipeda and the cubical symmetry replaced by symmetries represented by the triclinic, monoclinic, rhombic, or tetragonal systems in crystallography. Such a distortion of the cells might be expected to occur when there are many different kinds of atoms in the system. It may be impossible to arrange these so as to give complete cubical symmetry so that bodies with complicated constitutions would tend to crystallize in the more irregular systems.

The view we are discussing is supported by a comparison of the way in which elements of different valencies crystallize with the results indicated by the preceding table. The statements as to the forms in which the different elements crystallize are taken from Groth's *Chemische Krystallographie*, vol. i.

Monovalent Elements.

Very little seems to be known about the crystallization of the alkali metals; copper, silver, gold, which are monovalent, all crystallize in the regular system.

Divalent Elements.

Beryllium, magnesium, zinc, and cadmium all crystallize in the hexagonal system; an observation by Moissan suggests that calcium does so also; nothing is known as to the crystallization of barium and strontium.

Trivalent Elements.

Very little seems settled as to the crystallization of these elements, except that aluminium crystallizes in the regular system.

Quadrivalent Elements.

Carbon, silicon, and lead crystallize in the regular system, tin probably in a tetragonal one.

Pentavalent Elements.

Phosphorus crystallizes in the regular system; arsenic in two forms—one regular, the other trigonal.

Sexavalent Elements.

Sulphur crystallizes in several forms, monoclinic and rhombic; selenium is monoclinic or trigonal; tellurium trigonal.

Septavalent Elements.

Iodine crystallizes in a rhombic system.

Stability of the Distribution of Electrons.

Hitherto in considering the possible distribution of electrons we have only taken into account geometrical considerations; it is, however, of fundamental importance to consider the stability of the distribution, as no distribution is of any use for our purpose unless it is stable.

We shall begin with the case of a monovalent element when the electrons are at the corners of cubes and the atoms at the centre.

Take the origin of coordinates at one of the electrons and the axes parallel to the sides of a cube; let $2d$ be the length of a side of the cube.

Then the coordinates of the array of electrons are given by the equations

$$x = 2pd, \qquad y = 2qd, \qquad z = 2rd,$$

those of the atoms by

$$x = (2p+1)d, \qquad y = (2q+1)d, \qquad z = (2r+1)d,$$

where p, q, r may have any positive or negative integral values.

If the electron (p, q, r) has a vertical displacement ρ_{pqr}, the force due to this displacement tending to increase ρ_0, the displacement of the electron at the origin is

$$(\rho_0 - \rho_{p,q,r})\, B_{pqr},$$

where

$$B_{pqr} = \frac{e^2}{(2d)^3}\left(\frac{1}{(p^2+q^2+r^2)^{3/2}} - \frac{3r^2}{(p^2+q^2+r^2)^{5/2}}\right).$$

When the attraction between an atom and an electron separated by a distance r is expressed by

$$\frac{e^2}{r^2}\left(1 - \frac{c}{r}\right),$$

if the (p, q, r) atom has a vertical displacement $\omega_{p,q,r}$, the force tending to increase ρ_0, the displacement of the electron at the origin is

$$-(\rho_0 - \omega_{pqr})\, C_{pqr},$$

where

$$C_{p,q,r} = \frac{e^2}{d^3}\left\{\frac{1}{R_{pqr}^{3/2}} - \frac{3r^2}{R_{pqr}^{5/2}} - \frac{c}{d}\left(\frac{1}{R_{pqr}^{2}} - \frac{4r^2}{R_{pqr}^{3}}\right)\right\},$$

when

$$R_{pqr} = (2p+1)^2 + (2q+1)^2 + (2r+1)^2.$$

Thus if m be the mass of an electron

$$m\frac{d^2\rho_0}{dt^2}=\Sigma(\rho_0-\rho_{pqr})\,\mathrm{B}_{pqr}-\Sigma(\rho_0-\omega_{pqr})\,\mathrm{C}_{pqr}. \quad . \quad (1)$$

Since the electrons and the atoms are so distributed that if one of these has coordinates p, q, r, there are others whose coordinates are q, p, r, p, r, q, r, p, q, r, q, p, q, r, p, and since for such a group of six

$$\Sigma\left(\frac{1}{(p^2+q^2+r^2)^{3/2}}-\frac{3r^2}{(p^2+q^2+r^2)^{5/2}}\right)=0,$$

$$\Sigma\left(\frac{1}{(p^2+q^2+r^2)^2}-\frac{4r^2}{(p^2+q^2+r^2)^3}\right)=-\frac{2}{(p^2+q^2+r^2)^2},$$

$$\Sigma\,\mathrm{B}_{pqr}=0, \qquad \Sigma\,\mathrm{C}_{pqr}=-\Sigma\frac{2}{(p^2+q^2+r^2)^2}\times\frac{e^2}{d^3}\times\frac{c}{d}.$$

Thus equation (1) may be written,

$$m\frac{d^2\rho_0}{dt^2}=-\mathrm{A}\rho_0-\Sigma\,\rho_{pqr}\mathrm{B}_{pqr}+\Sigma\,\omega_{pqr}\mathrm{C}_{pqr},$$

where

$$\mathrm{A}=\frac{2c}{d}\frac{e^2}{d^3}\Sigma\frac{1}{(p^2+q^2+r^2)^2},$$

where p, q, r must all be odd.

If the disturbance is represented by

$$\rho=\cos\frac{2\pi}{\lambda_1}x\,.\cos\frac{2\pi}{\lambda_2}y\,.\cos\frac{2\pi}{\lambda_3}z,$$

we may put

$$\rho_{p,q,r}=\epsilon_1{}^p\,\epsilon_2{}^q\,\epsilon_3\;\rho_0,$$

where ϵ_1, ϵ_2, ϵ_3 are the roots, real and imaginary, of the equations

$$\epsilon_1{}^{\frac{\lambda_1}{2d}}=1, \qquad \epsilon_2{}^{\frac{\lambda_2}{2d}}=1, \qquad \epsilon_3{}^{\frac{\lambda_3}{2d}}=1,$$

and the equation for ρ_0 becomes,

$$m\frac{d^2\rho_0}{dt^2}=-\rho_0(\mathrm{A}+\Sigma\,\epsilon_1{}^p\,\epsilon_2{}^q\,\epsilon_3{}^r\,\mathrm{B}_{pqr})+\omega_0\Sigma(\epsilon_1{}^p\,\epsilon_2{}^q\,\epsilon_3{}^r\,\mathrm{C}_{pqr}). \quad (2)$$

To find the equation of motion of the atoms we must make some assumption as to the repulsion between two positive charges at a distance r; we shall suppose that this is expressed by

$$\frac{e^2}{r^2}-e^2f(r).$$

Then if M is the mass of an atom,

$$M\frac{d^2\omega_0}{dt^2}=-E\omega_0+\rho_0\Sigma(\epsilon_1^p\,\epsilon_2^q\,\epsilon_3^r\,C_{p\,.\,q\,.\,r}),$$

where

$$E=A+\Sigma F_{pqr}+\Sigma\epsilon_1^p\,\epsilon_2^q\,\epsilon_3^r\,(B_{pqr}+F_{pqr}),$$

and

$$F_{pqr}=\frac{f(r_{pqr})}{r_{pqr}}+\frac{r^2}{r_{pqr}}\frac{d}{dr_{p,\,q,\,r}}\left(\frac{f(r_{pqr})}{r_{pqr}}\right),$$

where r_{pqr} is the distance between the atom p, q, r and the atom whose displacement is ω_0.

As the mass of an atom is very large compared with that of an electron, an approximate solution for the motion of the electrons will be got by supposing that the atoms are not displaced; putting ω_0 equal to zero in equation (2) we get

$$m\frac{d^2\rho_0}{dt^2}=-\rho_0(A+\Sigma\epsilon_1^p\,\epsilon_2^q\,\epsilon_3^r\,B_{pqr}), \quad . \quad . \quad . \quad (3)$$

or, if ρ_0 varies as ϵ^{ipt},

$$mp^2=A+\Sigma\epsilon_1^p\,\epsilon_2^q\,\epsilon_3^r\,B_{pqr}:$$

this equation gives the frequency for all the types of vibration got by giving different values to ϵ_1, ϵ_2, ϵ_3. For the stability of the equilbrium all these frequencies must be real, *i. e.*

$$A+\Sigma\epsilon_1^p\,\epsilon_2^q\,\epsilon_3^r\,B_{pqr}$$

must be positive for all possible values of ϵ_1, ϵ_2, ϵ_3. The most likely vertical displacement to produce instability is when the displacement of each electron is equal and opposite to that of its nearest neighbours in a horizontal plane, while all electrons in the same vertical line have the same displacement. This is represented by putting $\epsilon_1=-1$, $\epsilon_2=-1$, $\epsilon_3=1$, and then

$$\Sigma\epsilon_1^p\,\epsilon_2^q\,\epsilon_3^r\,.\,B_{pqr}$$
$$=\frac{e^2}{8d^3}\Sigma(-1)^{p+q}\left(\frac{1}{(p^2+q^2+r^2)^{3/2}}-\frac{3r^2}{(p^2+q^2+r^2)^{5/2}}\right).$$

I have calculated the right-hand side by the method I have employed all through, *i. e.* by calculating the terms corresponding to the smaller values of p, q, r by arithmetic, while for the larger values of p, q, r I have supposed the electrons to be replaced by a uniform distribution of negative electricity of the same density as that due to the electrons, and calculated the effect of these by integration. I find, using arithmetic to calculate all the terms for which $p^2+q^2+r^2 \ngtr 30$, that

$$\Sigma \epsilon_1{}^p \epsilon_2{}^q \epsilon_3{}^r \mathrm{B}_{pqr} = -\frac{5 \cdot 2e^2}{8d^3}.$$

The value of A, *i. e.*

$$\frac{2c\,\epsilon^2}{d^4}\Sigma\left(\frac{1}{\{(2p+1)^2+(2q+1)^2+(2r+1)^2\}}\right)^2,$$

will depend upon the range over which we can use the expression

$$\frac{e^2}{r^2}\left(1-\frac{c}{r}\right)$$

for the force between a positive charge and an electron. It is certain that this expression cannot represent the force at distances which are considerable multiples of the atomic radii. We shall suppose that the expression holds for the atoms which are the nearest, next nearest, and next next nearest atoms to an electron, and that for the more distant atoms the force is represented by the inverse square law. The coordinates of the atoms which are the nearest neighbours to the electron are the permutations of $(\pm d, \pm d, \pm d)$ of the next nearest neighbours of $(\pm d, \pm d, \pm 3d)$ of the next next nearest neighbours $(\pm d, \pm 3d, \pm 3d)$; the value of A for this collection of atoms I find to be given by

$$\mathrm{A} = \frac{\cdot 384ce^2}{d^4}; \quad \ldots \ldots \quad (4)$$

hence, in order that $\mathrm{A}+\Sigma \epsilon_1{}^p \epsilon_2{}^q \epsilon_3{}^r \mathrm{B}_{pqr}$ should be positive and the equilibrium stable,

$$\frac{\cdot 384ce^2}{d^4} - \frac{5 \cdot 2e^2}{8d^3}$$

must be positive, *i. e.*

$$\frac{c}{d} > 1 \cdot 69.$$

The shortest distance between an atom and an electron is $\sqrt{3}\,d$ or $1 \cdot 724\,d$, hence the size of the cell for the equilibrium to be stable must be such that the distance between an atom and the nearest electron in the solid must not exceed c, the distance between the core of the atom and its electron when in the gaseous state, by more than a small fraction of this distance.

The value of d can easily be calculated, for if N is the number of atoms in unit volume of the substance, M the mass of an atom, and Δ the mass of unit volume of the solid,

$$\mathrm{N} \times (2a)^3 = 1 ; \quad \mathrm{NM} = \Delta ;$$

hence

$$8d^3 = \mathrm{M}/\Delta.$$

With this arrangement of electrons $1{\cdot}72 \times d$, where d is determined by the preceding equation, should be a close approximation to the distance of the electron from the centre in a gaseous atom.

The highest frequency vibration of the electrons is when the electrons are not displaced relatively to one another but only with respect to the atoms, in this case $\epsilon_1 = \epsilon_2 = \epsilon_3 = 1$, $\Sigma \epsilon_1 \epsilon_2 \epsilon_3 \mathrm{B}_{pqr} = 0$, and

$$\begin{aligned} mp^2 &= {\cdot}384 ce^2/d^4 \\ &= {\cdot}384 \times 8e^2(\Delta/\mathrm{M})\, c/d. \quad . \quad . \quad . \quad . \quad (5) \end{aligned}$$

As a vibrating system of electrons cannot transmit light of a higher frequency than the maximum free frequency of the system, this equation would give the value of the frequency of the shortest waves which could get through the crystalline medium.

This type of vibration is the one that would be excited by waves such as those of visible or ultra-violet light whose wave-length is large compared with the distance between the atoms in the solid. We might therefore expect evidence of it in the behaviour of monovalent solids when acted upon by light; the effect produced by light on such solids would be greatest when the frequency of the incident light was that given by equation (5). An interesting case when the action of light on a solid is a maximum for light of a particular wave-length is that known as the selective photo-electric effect (Hughes, 'Photo-Electricity,' chap. 5). This has been measured by Pohl and Pringsheim (*Verh. d. Deutsch. Phys. Ges.* xiii. p. 474 (1911)), and in the following table I give the comparison of the wave-lengths λ for which the effect is a maximum for the monovalent metals, sodium, potassium, rubidium, as determined by Pohl and Pringsheim, with the wave-lengths calculated by the equation (5), where c/d has the value 1·7, so that $mp^2=5{\cdot}224\,e^2\Delta/M$.

Metal.	Δ.	($M/1{\cdot}64\times10^{-24}$).	λ calculated.	λ observed.
Sodium	·971	23	3234	3400
Potassium...	·862	39	4457	4400
Rubidium ...	1·532	85·45	4940	4800

It will be noticed that the agreement is very satisfactory.

Specific Inductive Capacity of the Solid.

Let us suppose that a vertical electric force F acts on the solid, and that it displaces all the electrons through a distance ρ, and all the atoms through a distance z, then by equation (4) the force tending to restore the electron to equilibrium is $A(\rho-z)$; hence for equilibrium we must have

$$A(\rho-z)=Fe. \qquad (6)$$

If the distance between the electron and the atom is increased by $(\rho-z)$ each of the cells has an electric moment equal to $e(\rho-z)$, and the electric moment per unit volume will be $e(\rho-z)/8d^3$. If K be the specific inductive capacity of the solid this moment is $(K-1)F/4\pi$, hence

$$\frac{e(\rho-z)}{8d^3}=\frac{(K-1)F}{4\pi},$$

or by equation (6)

$$K-1=\frac{4\pi e^2}{8d^3A}=\frac{4\pi}{3{\cdot}07(c/d)}.$$

If p^2 is the limiting frequency given by (5) we see that

$$mp^2=\frac{4\pi e^2\Delta}{M(K-1)},$$

an expression from which c/d has been eliminated.

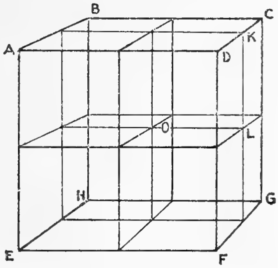
Potential Energy per unit volume of the Solid.

If the forces between all the electrical charges varied inversely as the square of the distance between them the potential energy per unit volume would be $\frac{1}{2}\Sigma(e_1e_2/r)$, where e_1, e_2 are two charges separated by a distance r and the summation is extended over all the charges in unit volume. In addition to the forces varying inversely as the square of the distance, there are forces between positive charges and electrons varying inversely as the cubes of the distance, and also forces which we have represented by $f(r)$ between the positive charges. It will be convenient to divide the potential energy up into two parts—one due to the forces varying inversely as the square of the distance, the other to the supplementary forces—and to calculate these parts separately.

Let us take first the potential energy possessed by a single electron; this is $e^2\Sigma(1/r)$, where the summation extends over all the other charges. If we try to calculate $\Sigma(1/r)$ by taking first the electrons and then the positive particles we get divergent series which are unmanageable; if, however, we regard the solid as built up of cubes with a unit positive charge at the centre and 1/8 of a unit negative charge at each of the eight corners, and, taking this as our unit, calculate the potential energy of the electron with reference to each of the cells, we get a series which rapidly converges and which can be calculated without great difficulty.

Suppose O is the electron for which we wish to calculate $\Sigma(1/r)$. O will be the meeting-place of eight cells, remove

Fig. 3.



these, leaving a cubical cavity around O. Then $\Sigma(1/r)$ will be the sum of terms due to the cells outside the cavity, plus the part due to the charges we have removed by taking away the eight cells. These charges were $-1/8$ at each of the eight corners, ABCDEFGH, $-1/4$ at each of the twelve points like K where two cells meet, and charges $-1/2$ at each of the six points like L where four of the cells which we have removed meet; in addition, there are the eight positive charges at the centres of the cubes which have been removed. The value of $e^2\Sigma\frac{1}{r}$ for these charges is, if $d=$ the side of a cube,

$$\frac{e^2}{d}\left(\frac{1}{\sqrt{3}}+\frac{3}{\sqrt{2}}+3-\frac{16}{\sqrt{3}}\right)=-3\cdot53\frac{e^2}{d}.$$

We shall indicate the various cells by the coordinates of their centres referred to O as origin and axes parallel to the sides of the cube. Thus, of the cubes outside the hollow, the nearest to the origin will be those whose centres have for coordinates the 24 permutations formed by $(\pm 1, \pm 1, \pm 3)\frac{d}{2}$, the next by $(\pm 1, \pm 3, \pm 3)$, and so on, the integers which occur being all odd integers.

The cells of the type (1, 1, 3)	furnish	$-{\cdot}0038\times 24\, e^2/d$.
(1, 3, 3)	,,	$+{\cdot}0014\times 24\, e^2/d$.
(1, 1, 5)	,,	$-{\cdot}0018\times 24\, e^2/d$.
(3, 3, 3	,,	$+{\cdot}0012\times 8\, e^2/d$.
(1, 3, 5)	,,	$-{\cdot}00006\times 48\, e^2/d$.
(3, 3, 5)	,,	$+{\cdot}0002\times 24\, e^2/d$.
(1, 1, 7)	,,	$-{\cdot}00026\times 24\, e^2/d$.
(3, 5, 5)	,,	$-{\cdot}00012\times 24\, e^2/d$.
(3, 1, 7)	,,	$-{\cdot}00020\times 24\, e^2/d$.
(3, 3, 7)	,,	$-{\cdot}00004\times 24\, e^2/d$.
. . . .		

Adding these to the preceding we find that $\Sigma ee'/r$ for the electron is

$$-3{\cdot}65\frac{e^2}{d}.$$

This will be the same as the value of $\Sigma\, ee'/r$ for the positive atom, for the arrangement of atoms and electrons may be represented either as a system of cubes with electrons at the corners and atoms at the centre, or a series with electrons at the centre and atoms at the corner; hence, if there are N atoms and N electrons per unit volume, the potential energy $\frac{1}{2}\Sigma\, ee'/r$ due to the forces varying inversely as the square of the distance will be

$$-3{\cdot}65\frac{\mathrm{N}e^2}{d}.$$

Now consider the part of the energy due to the forces varying inversely as the cube of the distance, and suppose that the supplementary forces between the atoms also varies according to this law. The potential energy due to forces varying inversely as the cube will for two charges ee' vary as $1/r^2$, where r is the distance between the charges; hence when we take the summation for all the charges per unit volume we shall get for the potential energy of unit volume an expression of the form

$$f\frac{\mathrm{N}e^2}{d^2},$$

where f is a positive quantity, since these supplementary forces are always in the opposite direction to the corresponding inverse square one. Hence the potential energy of a system containing N atoms will be expressed in the form,

$$-\mathrm{N}e^2\left(\frac{3{\cdot}65}{d}-\frac{f}{d^2}\right).$$

But, neglecting temperature effects, for the equilibrium to be stable d must have such a value that the quantity inside the bracket is a maximum, *i. e.*

$$-\frac{3{\cdot}65}{d^2}+\frac{2f}{d^3}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or

$$d=\frac{2f}{3{\cdot}65},$$

so that the potential energy of the system $=-1{\cdot}825\frac{e^2}{d}\mathrm{N}$.

Now let us find an expression for the work required to compress the solid so that d is changed from d to $d-\Delta d$; if the potential energy of the N atoms is denoted by u, the work required to compress them will be

$$\dot{u}\Delta d+\tfrac{1}{2}\ddot{u}(\Delta d)^2+\ldots,$$

where $\dot{u}$ is the first and $\ddot{u}$ the second differential of u with respect to d. But $\dot{u}=0$ and $\ddot{u}$ is equal to

$$-\mathrm{N}e^2\left(\frac{7{\cdot}30}{d^3}-\frac{6f}{d^4}\right)$$

$$=3{\cdot}65\frac{\mathrm{N}e^2}{d^3} \quad \text{by (7).}$$

Hence the work required to compress the cells is

$$\tfrac{1}{2}\,3{\cdot}65\,.\,\frac{\mathrm{N}e^2}{d^3}(\Delta d)^2;$$

if V denotes the volume occupied by these cells

$$\frac{\Delta d}{d}=\frac{1}{3}\frac{\Delta \mathrm{V}}{\mathrm{V}};$$

hence the work $=\dfrac{1}{2}\dfrac{3{\cdot}65}{9}\dfrac{\mathrm{N}e^2}{d}\left(\dfrac{\Delta \mathrm{V}}{\mathrm{V}}\right)^2;$

but if k is the bulk modulus this work is equal for unit volume to

$$\tfrac{1}{2}k\left(\frac{\Delta V}{V}\right)^2;$$

hence $$k=\frac{3\cdot 65}{9}\frac{Ne^2}{d},$$

where N is the number of atoms per unit volume.

If M is the mass of an atom and Δ the density,

$$NM=\Delta \quad \text{and} \quad N(d)^3=1,$$

hence $$k=\frac{3\cdot 65}{9}e^2\left(\frac{\Delta}{M}\right)^{4/3}. \quad \ldots \ldots \quad (8)$$

The comparison of the values for k given by (8) for the monovalent alkali metals with their values as determined by Richards' very valuable experiments (Kaye and Laby's Tables) is given in the following table :—

Metal.	Δ.	$M/1\cdot 64\times 10^{-24}$.	k calculated.	k observed.
Lithium......	·534	7	$\cdot 14 \times 10^{12}$	$\cdot 114\times 10^{12}$
Sodium	·971	23	$\cdot 068\times 10^{12}$	$\cdot 065\times 10^{12}$
Potassium ...	·862	37	$\cdot 03 \times 10^{12}$	$\cdot 032\times 10^{12}$
Rubidium ...	1·532	85·5	$\cdot 022\times 10^{12}$	$\cdot 025\times 10^{12}$
Cæsium	1·87	132	$\cdot 016\times 10^{12}$	$\cdot 016\times 10^{12}$

Thus the absolute values of k and not merely the relative ones are in very close agreement.

If we take the cell with charges 1/8 at its corners and the atom at its centre as the unit, the potential energy corresponding to each cell is $-1\cdot 82\, e^2/d$. When the solid is changed into a monatomic gas, each of these cells becomes an atom whose energy is $-\frac{1}{2}e^2/c$. Thus to convert N atoms of a monovalent solid into a monatomic gas requires the expenditure of

$$Ne^2\left(\frac{1\cdot 82}{d}-\frac{1}{2c}\right)$$

units of work, or, if $2c/d=1\cdot 7$,

$$=Ne^2\frac{1\cdot 24}{d}.$$

If N is the number of atoms in a gramme $NM=1$, and $d^3=M/\Delta$; hence the work required to convert 1 gramme of the solid into a monatomic gas is, neglecting the difference in the specific heats,

$$e^2 \, 1{\cdot}24 \, . \, \frac{\Delta^{1/3}}{M^{4/3}} .$$

If M' is the atomic weight of the atom whose mass is M,

$$M = M' \times 1{\cdot}64 \times 10^{-24},$$

and the preceding expression becomes,

$$1{\cdot}45 \times 10^{12} \frac{1}{M'} \left(\frac{\Delta}{m'} \right)^{1/3} .$$

The energy $1{\cdot}825 \, e^2/d$ possessed by an atom in the solid state with its electron is equal to that acquired by a charge e falling through $21{\cdot}25 \left(\frac{\Delta}{M'} \right)^{1/3}$ volts.

Latent Heat of Fusion of Monovalent Elements.

If the energy per atom in the liquid state is greater than that in the solid the transformation of each atom from the solid to the liquid state will involve the expenditure of a definite amount of energy. This, when there is no difference in the specific heats for the two states, will be a measure of the latent heat of fusion.

The energy per atom when these are at the centres of cubes whose edge is d is represented by

$$-1{\cdot}82 \, . \, \frac{e^2}{d} \, ;$$

if M' is the atomic weight and Δ the density, this is equal to

$$-34 \, . \, 10^{-12} \left(\frac{\Delta}{M'} \right)^{1/3} ;$$

the energy per gramme is

$$-\frac{20{\cdot}7 \times 10^{12}}{M'} \left(\frac{\Delta}{M'} \right)^{1/3} ; \quad . \quad . \quad . \quad . \quad . \quad (9)$$

hence if Δ' is the density in the liquid state, the difference in energy between one gramme of solid and one of liquid is

$$\frac{20{\cdot}7 \times 10^{12}}{M'} \left\{ \left(\frac{\Delta}{M'} \right)^{1/3} - \left(\frac{\Delta'}{M'} \right)^{1/3} \right\} .$$

For potassium $M' = 39$, the values of Δ, Δ', as determined by Vicontini and Omodei (Landolt and Börnstein *Tabellen*), are

$$\Delta = \cdot 851, \qquad \Delta' = \cdot 8298.$$

Substituting these values, we find that the difference between the energy of one gramme of potassium in the solid and liquid state is 28 calories, the latent heat of fusion as found by experiment is 16. We have neglected any effect due to the alteration of the specific heats, and Δ and Δ' are so close together that a small percentage error in either would produce a large error in their difference.

We have hitherto confined our attention to cells in the interior of the solid; let us consider what are the conditions of a cell at the surface.

A corner of a cell on the surface is the meeting-place of only four cells ; thus only four corners coalesce, and as each corner only carries 1/8 of a charge, the total charge would be 1/2. Now the charge on an electron is the smallest that can exist, so that we cannot represent the state of the surface by placing electrons at the corners of the cells. We must replace this distribution by one where the number of electrons is only one-half that of the corners of the cells, *i. e.*, one-half of the number of atoms in the cells at the surface. One symmetrical way of distributing the electrons is, if ABCDEFGHIJKL represent the atoms below the surface

A	B	C
D	E	F
G	H	I
J	K	L

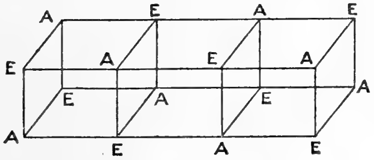
layer of electrons, to put electrons over BDFHJL but not over ACEGIK.

We must now consider the forces acting on the surface electrons. Starting from the top of the crystal, we have first a layer of electrons with $N/2$ electrons per unit area; next below this we have a layer of positively charged atoms with N atoms per unit area; following this we have a layer of electrons with N electrons per unit area; and so on. The excess of positive over negative electricity in all the layers below the surface is the amount of electricity in a layer of atoms when there are $N/2$ atoms per unit area.

If, as a first approximation, we suppose that the effect of the charges carried by the atoms and electrons in the various layers is the same as if the amount of electricity in the layer instead of being concentrated at points were uniformly distributed over the layer, the electric force produced by the electricity below the surface layer of electrons would be an attraction equal to $2\pi\sigma$, where σ is the surface density of the layer when there are N/2 atoms per unit area. Hence, if d be the distance between two atoms, $\sigma = e/2d^2$; hence the force acting on each surface electron is $\pi c^2/d^2$. This is the attraction due to the forces varying inversely as the square of the distance; it must be balanced by the repulsive force varying inversely as the cube of the distance which the atoms exert on the electrons. If we suppose that the distance between the surface layer of electrons and the layer of atoms immediately beneath them is the same as that in the body of the crystal between a layer of electrons and the adjacent layer of atoms, we find that the repulsive force is greater than $\pi e^2/d^2$, the attractive one. The upper layer of electrons will hence move further away from the atoms, so that the distance of the electrons in the outer layer from the nearest atoms is greater than it is for the electrons in the interior. Thus the potential energy of an atom on the surface will be greater than that of an atom in the interior; as the atoms on the surface have an abnormally large amount of energy, there will be in the expression for the energy of the solid a term proportional to the surface. This term will be proportional to the surface tension, so that the surface tension possessed by the substance can be calculated. I must leave this, however, for another occasion.

Another possible way of arranging the atoms and the electrons when they are equal in number is that shown in fig. 4, where the A's represent atoms and the E's electrons.

Fig. 4.



We shall consider the conditions for stability and the properties of this system.

Let us take the coordinate axes parallel to the axes of the lattices, and the origin at an electron. The electrons may be divided into two classes: in the first class the coordinates of the electrons are represented by the equations

$$x = pd, \quad y = qd, \quad z = rd,$$

where p, q, r are all even and d is the shortest distance between an atom and an electron; in the second class they are represented by the equations

$$x = pd, \quad y = qd, \quad z = rd,$$

where two of the three integers are odd and the third even. The atoms are represented by

$$x = pd, \quad y = qd, \quad z = rd,$$

where p, q, r must either all be odd or two even and one odd.

We shall suppose that the displacements of the atoms may be neglected. We shall denote a displacement parallel to z of an electron of the first type by ρ, those of the second type by ρ'. If we wish merely to investigate the stability, it will be sufficient to confine our attention to the case which is most likely to be unstable. A little consideration will show that this is the one where the displacement of any electron is equal and opposite to that of its nearest neighbours in the plane at right angles to the direction of displacement. This will be the case if all the ρ displacements are the same and if the ρ' displacements are equal and opposite to the ρ ones in the plane of xy and in all parallel planes whose distance from xy is an even multiple of d, while in those in which the distance is an odd multiple of d the ρ and ρ' are equal both in sign and magnitude.

In this case the force tending to increase ρ due to the repulsion of the other electrons is equal to

$$\frac{2\rho e^2}{d^3}\Sigma\left(\frac{1}{(p^2+q^2+r^2)^{3/2}}-\frac{3r^2}{(p^2+q^2+r^2)^{5/2}}\right),$$

where p and q must both be odd and r even. I find by a combination of arithmetic and integration that the quantity inside the bracket is equal to 1·04, so that the disturbing force due to the electrons is $\frac{2{\cdot}08\rho e^2}{d^3}$.

Consider, now, the restoring effect due to the attraction of the positive atoms. Owing to the symmetry of their distribution round the electron, no term arises from the part of the force which varies inversely as the square of the distance; the whole effect is due to the part varying inversely as the cube of the distance, and if we limit, as before, the effect of this to the atoms which are nearest, next nearest, and next next nearest to the electron the restoring force is

$$\rho\left(\frac{2e^2c}{d^4}+\frac{8}{27}\frac{e^2c}{d^4}+\frac{8}{25}\frac{e^2c}{d^4}\right) = 2\cdot62\,\rho\,.\frac{e^2c}{d^4}.$$

Hence the equation for ρ is

$$m\frac{d^2\rho}{dt^2}=-\rho\frac{e^2}{d^3}\left(2\cdot62\,.\frac{c}{d}-2\cdot08\right);$$

so that for the equilibrium to be stable,

$$\frac{c}{d}>\frac{2\cdot08}{2\cdot62}>\cdot79.$$

The frequency p of the greatest vibration is given by the equation

$$mp^2 = 2\cdot62\frac{e^2}{d^3}.\frac{c}{d}.$$

To express d in terms of M and Δ, the molecular weight and density of the solid, we notice that the atoms may be arranged in face-centred cubes with a side $2d$, and that each of these cubes will contain four atoms. Hence the number of atoms in unit volume is $4\times(1/8d^3)$, and this equals Δ/M. Hence $\frac{1}{d^3}=\frac{2\Delta}{\mathrm{M}}$; so that the critical frequency is given by

$$mp^2 = 5\cdot24\,.\,\frac{\Delta}{\mathrm{M}}\frac{c}{d}.$$

If as in the case considered on p. 732 the shortest distance between an atom and an electron is much the same in the solid and gaseous state, c/d will be nearly unity, so that

$$mp^2 = 5\cdot24\frac{\Delta}{\mathrm{M}}e^2 \text{ approximately.}$$

This is practically identical with the critical frequency for the other arrangement of electrons, so that the selective photo-electric effect will not distinguish between them.

We proceed to consider the value of the bulk modulus given by the new arrangement. We calculate, as before, the potential energy of the system of electrons and atoms. We divide the system up in cells, but now the cells, instead of being cubes with electrons at the corners and atoms at the centre, are face-centred cubes whose side is equal to $2d$ and which have atoms at the middle points of the sides and also at the centre. I find in this way that the potential energy due to the forces varying inversely as the square of the distance is, for N atoms and N electrons,

$$-\mathrm{N}\,.\,1{\cdot}77\frac{e^2}{d}.$$

It follows, as on p. 735, that the bulk modulus will be given by

$$k = \mathrm{N}\,.\,\frac{1{\cdot}77}{9}\,\frac{e^2}{d},$$

where N is the number of atoms per unit volume.

Since $\mathrm{N}=\frac{\Delta}{\mathrm{M}}$ and $\frac{1}{d}=\left(\frac{2\Delta}{\mathrm{M}}\right)^{1/3}$,

$$k = \frac{2{\cdot}2e^2}{9}\left(\frac{\Delta}{\mathrm{M}}\right)^{4/3}.$$

This is not much more than half the value for the previous arrangement, which agreed exceedingly well with experiment. Hence we conclude that the arrangement we have just been discussing does not represent that of the alkali metals, while the distribution with one atom at the centre of a cube of eight electrons does so.

Compressibility of a trivalent element.

We proceed to test the theory by taking another case where the distribution of electrons is of a different character from either of the preceding cases.

A trivalent element when in a solid state must have the atoms and electrons arranged so that there are three electrons for each atom. If the solid crystallizes in the regular system this will require each atom to be surrounded by a rhombic dodecahedron of electrons. When these dodecahedra are packed together so as to fill space, the arrangement can be seen to be equivalent to any one of the following:—

1. A system of cubical cells with the atoms at the corners of the cube and also at the centre of its faces. The electrons are arranged (*a*) at the middle points of the edges of the cube, (*b*) at the centre of the eight cubes into which the larger cube is divided by planes bisecting its edges at right angles, (*c*) an electron at the centre of the large cube. This arrangement gives the equivalent of four atoms per cell: the electrons at the middle points of the edges are equivalent to 3, those at the centre of the little cubes 8; these with the one at the centre of the large cube make 12—three times the number of atoms.

2. Another equivalent arrangement is a system of cubical cells with electrons at the corners and the centres of the faces and at the centres of each of the eight cubes into which the larger cube is divided : the atoms are at the middle points of the edges of the large cube, and one is at the centre of the large cube. The electrons at the corners of the cube in this arrangement correspond to the octahedral electrons.

3. An arrangement with the electrons at the corners, the centres of the edges and the centre of a cube, and at the centres of half the eight small cubes into which the larger cube is divided : the atoms are placed at the centres of the four little cubes not occupied by the electrons. The centres are chosen so that both the electrons and atoms are at the corners of regular tetrahedra—the electrons on the outside of the cube with this arrangement corresponding to the cubical electrons on the dodecahedron.

To calculate the compressibility we proceed, as before, by calculating $\Sigma\frac{e_r e_\rho}{r}$ for each type of atom and electron. Starting with the positive atom, the arrangement 1 affords the easiest means of calculating $\mathrm{E}\Sigma\frac{e}{r}$, where E is the charge on a positive atom and r the distance of the charge e from E. Putting $\mathrm{E}=3e$, I find this sum is equal to $-\frac{e^2}{d}43\cdot2$, where d is a side of the large cube.

For an octahedral electron, using the arrangement 2 for calculation, I find the corresponding quantity to be $-\frac{e^2}{d}.1$.

For a cubical electron, using arrangement 3 for calculation, the corresponding quantity is $-\frac{e^2}{d}.7\cdot2$.

Each atom is associated with one octahedral electron and two cubical ones, so that the value for N atoms with their associated electrons is

$$-\tfrac{1}{2}\mathrm{N}\frac{e^2}{d}(43\cdot2+\cdot1+14\cdot4)=-\mathrm{N}\frac{e^2}{d}(28\cdot8).$$

If N is the number of atoms per unit volume, M the mass of an atom,

$$\mathrm{NM}=\Delta,$$

where Δ is the density of the substance.

Since there are four atoms in each cube whose side is d,

$$\mathrm{N}=\frac{4}{d^3}\quad\text{or}\quad\frac{1}{d}=\left(\frac{\Delta}{4\mathrm{M}}\right)^{1/3}.$$

Hence the potential energy per unit volume due to the forces varying inversely as the square of the distance is

$$-28{\cdot}8e^2\frac{1}{4^{1/3}}\left(\frac{\Delta}{M}\right)^{4/3};$$

so that (see p. 735) the bulk modulus will be

$$\frac{28{\cdot}8}{9}\frac{e^2}{4^{1/3}}\left(\frac{\Delta}{M}\right)^{4/3}.$$

Aluminium is a trivalent element, which crystallizes in the regular system; for this metal, Δ/M is equal to $2{\cdot}65/27\times6{\cdot}4\times10^{-24}$. Substituting this value in the preceding expression, we find that the value of the bulk modulus is $\cdot98\times10^{12}$; the value found by experiment is $\cdot78\times10^{12}$.

The limiting frequency of the vibrations of the electrons.

Following the method used for the monovalent elements, I find that the limiting period for the vibrations of the octahedral electrons is given by the equation

$$mp^2 = 32{\cdot}88\,e^2\frac{\Delta}{M}\frac{c}{d},$$

and that of the cubical electrons by

$$mp^2 = 36{\cdot}9\,e^2\frac{\Delta}{M}\frac{c}{d},$$

where

$$\frac{1}{d^3}=\frac{\Delta}{4M}.$$

The stability of the system requires that c/d should be greater than ·3. If we compare these expressions with that for sodium, and remember that Δ/M for aluminium is 2·4 times that for sodium, we see that the wave-length of the critical frequency for aluminium will be less than 1700 A.U., *i. e.* far up in the ultra-violet. Thus it is only in this region that we should expect to find evidence of the selective photo-electric effect with aluminium.

Electrons arranged in face-centred cubes.

With this arrangement the number of electrons is four times the number of atoms. As this is the proportion between the atoms and electrons in all binary compounds which satisfy the ordinary conditions of valency, its investigation is of exceptional importance.

Stability of the arrangement.

Take the origin of coordinates at the corners of one of the cubes, the axes parallel to the sides of the cube. Let $2d$ be a side of the cube. Then the coordinates of the corners of the cubes are given by

$$x = pd, \quad y = qd, \quad z = rd,$$

where p, q, r are even integers.

The coordinates of the centres of the faces are given by

$$x = pd, \quad y = qd, \quad z = rd,$$

where two out of the integers p, q, r are odd and the third even.

The coordinates of the atoms are given by

$$x = pd, \quad y = qd, \quad z = rd,$$

where p, q, r are all odd.

Consider a displacement of the electrons parallel to the axis of z, such that all the electrons of one type have the same displacement. Let ρ_1, ρ_2, ρ_3 be the displacement of the electrons forming the corners of the cube, the centres of the faces parallel to xy, and the centres of the other faces respectively.

The force tending to increase ρ_1, due to the displacement ρ_2, is

$$(\rho_1 - \rho_2)\frac{e^2}{d^3}\Sigma\left(\frac{1}{(p^2+q^2+r^2)^{3/2}} - \frac{3r^2}{(p^2+q^2+r^2)^{5/2}}\right)$$

for all odd values of p and q and even values of r.

The summation I find to be 1·1. The force tending to increase ρ_1 may thus be written

$$a(\rho_1 - \rho_2),$$

where

$$a = 1{\cdot}1\frac{e^2}{d^3}.$$

Let us now consider the force tending to increase ρ_1 due to the displacements ρ_3. If ρ_2 is equal to ρ_3, then the symmetrical system formed by the whole of the electrons at the centre of the faces will not produce any force tending to increase ρ_1; hence the force due to the displacement ρ_3 tending to increase ρ_1 is

$$-a(\rho_1-\rho_3).$$

The total force tending to increase ρ_1 is thus

$$a(\rho_3-\rho_2)\;;$$

the force tending to increase ρ_2 is

$$a(\rho_2-\rho_1)\;;$$

and that tending to increase ρ_3 is

$$a\left(\frac{\rho_1+\rho_2}{2}-\rho_3\right).$$

The force due to the positive charges tending to diminish ρ_1 if E is the positive charge of the atom is $\beta_1\rho_1$ when

$$\beta_1=\mathrm{E}e\left(\frac{8}{27}\frac{c}{d^4}+\frac{8}{121}\frac{c}{d^4}+\frac{8}{361}\frac{c}{d^4}\right),$$

where the effect of the force varying inversely as the cube of the distance is supposed to be confined to the nearest, next nearest, and next next nearest atoms.

The effect of the force varying inversely as the square of the distance exerted by the positive atoms is proportional to

$$\Sigma\left(\frac{1}{(p^2+q^2+r^2)^{3/2}}-\frac{3r^2}{(p^2+q^2+r^2)^{5/2}}\right)$$

for all odd values of p, q, r, and therefore vanishes.

The force tending to diminish ρ_2 due to the positive atoms is $\beta_2\rho_2$, where

$$\beta_2=\frac{\mathrm{E}e}{d^3}\left(6\frac{c}{d}-\frac{8}{125}\frac{c}{d}-3{\cdot}77\right)$$
$$=\frac{\mathrm{E}e}{d^3}\left(5{\cdot}96\frac{c}{d}-3{\cdot}77\right).$$

The effect of the force varying inversely as the square of the distance is

$$\frac{\mathrm{E}e}{d^3}\Sigma\left(\frac{1}{(p^2+q^2+r^2)^{3/2}}-\frac{3r^2}{(p^2+q^2+r^2)^{5/2}}\right)$$

for all odd values of r and even values of p and q. The sum under these conditions is $-3{\cdot}77$.

The force due to the positive charge tending to diminish ρ_3 is $\beta_3\rho_3$, where

$$\beta_3=\frac{\mathrm{E}e}{d^3}\left(1{\cdot}88-1{\cdot}75\frac{c}{d}\right).$$

The equations of motion are

$$m\frac{d^2\rho_1}{dt^2} = a(\rho_3-\rho_2)-\beta_1\rho_1,$$

$$m\frac{d^2\rho_2}{dt^2} = a(\rho_3-\rho_1)-\beta_2\rho_2,$$

$$m\frac{d^2\rho_3}{dt^2} = a\left(\frac{\rho_1+\rho_2}{2}-\rho_3\right)-\beta_3\rho_3,$$

if ρ_1, ρ_2, ρ_3 are proportional to e^{ipt}; p is given by the equation

$$\begin{vmatrix} mp^2-\beta_1, & -a, & a \\ -a, & mp^2-\beta^2, & a \\ \frac{a}{2}, & \frac{a}{2}, & mp^2-a-\beta_3 \end{vmatrix} = 0.$$

Putting $mp^2=xe^2/d^3$ and $y=c/d$, we find when $E=4e$ that

$$x^3-x^2(15{\cdot}3y-6{\cdot}44)+x(290{\cdot}16y-121{\cdot}16y^2-133)$$
$$-y(474y-252y^2-204)=0.$$

For stability the values of x given by this equation must be real and positive; for this to be so, the constant term and the coefficient of x^2 in the cubic must be negative and the coefficient of x positive. This will be the case if y is between ·71 and 1·17. The shortest distance between the atom and an electron is d; hence for equilibrium the distance must be between 1·4c and ·85c.

If the atoms are different, as in a binary compound AB, we may have an atom with one charge inside one cell and an atom with another charge inside another. It is easy to see, however, that if the atoms are arranged according to the scheme below—

B A B A
A B . A B
B A B A,

the expressions we have obtained will hold provided the sum of the positive charges on the atoms A and B is equal to 8, which is the relation when the compound obeys the ordinary valency conditions.

Specific Inductive Capacity.

If the external electric force F parallel to z acts on the medium, the displacements ρ_1, ρ_2, ρ_3 relative to the positive atoms of the three types of electrons are given by the equations

$$\begin{aligned} a(\rho_3-\rho_2)-\beta_1\rho_1 &= -\mathrm{F}e, \\ a(\rho_3-\rho_1)-\beta_2\rho_2 &= -\mathrm{F}e, \\ \frac{a}{2}(\rho_1+\rho_2-2\rho_3)-\beta_3\rho_3 &= -\mathrm{F}e. \end{aligned}$$

The solution of these equations is

$$\begin{aligned} \rho_1 &= \mathrm{F}e(\beta_3+2a)(\beta_2-a)/\Delta, \\ \rho_2 &= \mathrm{F}e(\beta_2+2a)(\beta_1-a)/\Delta, \\ \rho_3 &= \mathrm{F}e\left(\beta_1\beta_2-\frac{a}{2}\right)(\beta_1+\beta_2)/\Delta, \end{aligned}$$

where

$$\Delta = \begin{vmatrix} \beta_1, & a, & -a, \\ a, & \beta_2, & -a, \\ -\frac{a}{2}, & -\frac{a}{2}, & \beta_3-a \end{vmatrix}.$$

The electrical moment of each cell due to these displacements is

$$(\rho_1+\rho_2+2\rho_3)e.$$

The number of cells per unit volume is $1/8d^3$. Hence the electrical moment per unit volume is

$$(\rho_1+\rho_2+2\rho_3)\frac{e}{8d^3},$$

and if K is the specific inductive capacity this is equal to

$$\frac{\mathrm{K}-1}{4\pi}\,.\,\mathrm{F}.$$

Substituting the values for ρ_1, ρ_2, ρ_3, we find

$$\frac{\mathrm{K}-1}{4\pi}=\frac{1}{8y}\frac{(263{\cdot}4y-105y^2-109)}{(474y-252y^2-204)},$$

where $y=c/d$ and must be between ·71 and 1·17.

Substituting the permissible values of y, we find that the specific inductive capacity of solids possessing this structure would be greater than four; so that it is only substances with a high refractive index which can have their electrons arranged in this way.

Value of the bulk modulus.

This can be calculated if we know the value of $\Sigma\, e_r e_s/r$ for the system. To make the calculation, consider first the value of the contribution made by one of the electrons at the corners of the cube to this sum. Let A be such a corner. We suppose the medium built up of face-centred cubes: remove the eight that meet at A, and calculate separately the contributions the charges so removed would have made to the sum; then treat each of the remaining cells as a unit, and calculate the contribution of each of these. This contribution diminishes very rapidly as the distance from the electron increases. In this way we find that the value of the sum of the terms $\Sigma\, e_r e_s/r$ which contain this corner electron is $-4{\cdot}5 e^2/\mathrm{D}$, where D is a side of the cube. Now consider the contribution to the sum of one of the electrons at the centre of a face. Proceeding by a similar method, I find this equal to $-3{\cdot}2\, e^2/\mathrm{D}$; while the contribution of a positively-charged atom is $-52{\cdot}6\, e^2/\mathrm{D}$.

As the charges carried by the electrons at the centre of the faces is three times that carried by the electrons, the value of $\Sigma\, e_r e_s/r$ for N cells is equal to

$$-\tfrac{1}{2}(4{\cdot}5+3\times 3{\cdot}2+52{\cdot}6)e^2/\mathrm{D},$$

i. e. to $-33{\cdot}35\, e^2/\mathrm{D}$.

From p. 735 we see that this will correspond to a bulk modulus k given by the equation

$$k=\frac{33{\cdot}35}{9}e^2\left(\frac{\Delta}{\mathrm{M}}\right)^{4/3}.$$

So that for similar values of Δ/M the bulk modulus with this arrangement of electrons is about nine times that for the alkali metals.

For the diamond for which $\Delta=3{\cdot}52$ the value of the bulk modulus deduced from this formula is $8{\cdot}1\times 10^{12}$. This is much higher than the value 2×10^{12} obtained by Richards for carbon in the form of diamond. Richards puts a question mark after this value, so that it may be inferred that there is more uncertainty about this value than about those of the other elements. The very high value for the diamond given by the formula is due not merely to the value of the coefficient but to the abnormally high value of Δ/M for the diamond—a value far in excess of that for any other element.

In this investigation we have supposed that each carbon atom acts as a separate and independent unit. There is considerable evidence, however, that the atoms in the diamond are arranged in groups. If so, it may be necessary to take the group as the unit rather than the atom; this would indicate that when the diamond is compressed the compression is effected more by bringing the groups together than by diminishing the distance between the atoms in a group. This grouping of the atoms would seriously modify the expression for the bulk modulus, for we have to replace Δ/M by Δ/nM, where n is the number of atoms in a group. This will diminish the value of k in the proportion of 1 to $n^{4/3}$: thus if there were three carbon atoms grouped together in the diamond, k would be $8{\cdot}1/3^4$ or $1{\cdot}9\times10^{12}$; if there were four the value $1{\cdot}3\times10^{12}$, values which are much more consistent with Richard's results than that deduced on the assumption that the atoms were not grouped.

A point of considerable interest with regard to the constitution of salts is raised by the value of the compressibility for electrons arranged in a space-centred cube; if all the movable electrons go into the walls of the cell the space-centred cube would be the cells enclosing the atoms in a binary valency compound, since in these compounds there are eight electrons for the two atoms. The value we have obtained for k shows that if this were the case these compounds would be characterized by small compressibility and consequently high boiling-points: the oxides answer to this description, the chlorides certainly do not. Though the k has been determined for few simple compounds, its value for NaCl and for KCl has been determined by Voigt, Röntgen, and Richards. The results are given in the following table; the last column gives the value calculated by the preceding formula.

	Δ.	k observed.	k calculated.
NaCl	2·1	$\cdot23\times10^{12}$	$1{\cdot}2\times10^{12}$
KCl	1·99	$\cdot192\times10^{12}$	$\cdot76\times10^{12}$

It will be noticed that the values for the chlorides indicated by the theory are far in excess of those found by experiment.

The actual values are comparable with those which would be obtained from the formula (8) on p. 736, which corresponds to the case of simple cubical cells with a single positive charge at the centre of each. This suggests that the structure of the chloride cells is not a face-centred cube with a singly-charged sodium atom in one cell and a chlorine atom with a positive charge of 7 in the adjacent ones, but that the chlorine atom instead of losing all its seven electrons to form the outer walls of the cell only uses one, and the other six electrons and the atom with seven charges form a unit having unit positive charge ; so that the structure of the cell for sodium chloride would be represented by a sodium atom at the centre of one cell and a chlorine atom surrounded by six electrons arranged as a regular octahedron considerably smaller than the cube at the centres of adjacent cells. This arrangement is in some respects more symmetrical than the other, for in it we have what is equivalent to a unit positive charge at the centre of each cell ; in the other arrangement there is a unit positive charge in one cell and a positive charge of seven in the adjacent cell. Thus an electron at the centre of a face would be pulled one way by a charge of seven and in the opposite way by a charge of one. The result would be that the electron would be displaced ; the face-centred cubes would become cubes with pyramids on their faces, the pyramids being convex for one set of tubes and concave for the other.

If we regard the chlorine cell as equivalent to a monovalent one, we can find the difference between the energy of a gramme molecule of sodium chloride and the energy of the sodium and chlorine before combination.

By the equation (9) on p. 737 the energy of 23 grammes of sodium is

$$-2{\cdot}07\times10^{13}\left(\frac{\Delta}{23}\right)^{1/3},$$

where $\Delta = {\cdot}971$ is the density of metallic sodium. Thus the energy of the sodium before combination is

$$-2{\cdot}07\times{\cdot}348\times10^{13} ;$$

after combination the energy is

$$-2{\cdot}07\times10^{13}\left\{\frac{2\Delta_1}{23+35{\cdot}5}\right\}^{1/3},$$

where $\Delta_1 = 2{\cdot}17$ is the density of sodium chloride. The energy after combination is thus

$$-2{\cdot}07\times{\cdot}4213\times10^{13}.$$

The energy of the chlorine before combination is

$$-2{\cdot}07\left(\frac{\Delta_2}{35{\cdot}5}\right)^{1/3},$$

where Δ_2 is the density of liquid chlorine, $\Delta_2 = 1{\cdot}558$ at

$-33°$ C. Hence the energy of the liquid chlorine before combination is

$$-2·07\times·353\times10^{13};$$

after combination it is the same as that of the sodium. Hence the change in energy is

$$2·07\times10^{13}(2\times·4213-·348-·353)$$

$$=2·07\times10^{13}\times·142 \text{ ergs},$$

or about 70,000 calories.

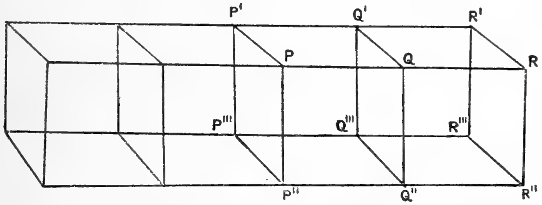
The heat of combination for sodium and gaseous chlorine is $97·8\times10^3$. If we subtract the correction given by Richards of 18,000 calories for the vaporization of the liquid chlorine, the heat produced when liquid chlorine combines with sodium would be about 80,000 calories; so that the theoretical and experimental results are in fair agreement.

An interesting point in connexion with the energy of a crystallized solid compound is whether all the atoms in a compound are equally spaced, or whether some may be regarded as collected in a group and more intimately connected together than the others. Chemists have introduced the conception of radicles such as CN, CH_3, C_2H_5, CH, which play the same part in chemical reactions as the atoms of monovalent or divalent atoms. The question is whether in a solid crystalline compound containing these radicles their atoms act as a single group, or whether each of their atoms occupies a separate cell. This question could be answered by a determination of the compressibility of the compound. Thus, take the compound KCN as an example: are there separate cells for the atoms of K, C, N—*i. e.*, are there three cells for each molecule, or are the C and N atoms paired together in a single cell so that each molecule of KCN furnishes two cells instead of three? The atomic volume of KCN is 42·8: if there are three cells the volume of each cell will be 14·3, if there are two it will be 21·4. The compressibility of the substance diminishes with the size of the cell; the larger cell would give a compressibility not very different from sodium, the smaller one a compressibility less than two-thirds of this value. I cannot, however, find any record of the compressibility of KCN. Take ammonium chloride, NH_4Cl, as another example. The atomic volume is 35·2: if NH_4 forms a group at the centre of one cell each molecule of NH_4Cl will furnish two cells, each having an atomic volume of 17·6 intermediate between the volumes of the cells in solid lithium and sodium and giving a compressibility between the values for those substances; if, however, each of the six atoms in NH_4Cl had a separate cell the volume of each would be 5·8. This is small compared with that of the cells in any of the chlorides of the alkali metals; so that NH_4Cl would have an abnormally small compressibility compared with any of these salts. Though no determinations of the compressibility of NH_4Cl have been published, there seems nothing to indicate that its compressibility is abnormally small; if it is not, then ammonium, NH_4, must behave like a single atom in NH_4Cl.

Stability of chains of atoms.

The possibility of atoms being linked together in long chains is interesting from the point of view of organic chemistry. We shall consider the case of a chain when the electrons are arranged like a line of cubical boxes placed end to end (fig. 5); the positively charged atoms are at the centres of the cubes. The chain is supposed to be of infinite length.

Fig. 5.



Consider first the forces exerted by the electrons on each other.

The force in the direction $P''P$ on an electron P, due to the other electrons, will, if a is the side of one of the cubes, be

$$\frac{e^2}{a^2}\left\{1+2\left(\frac{1}{2^{3/2}}+\frac{1}{5^{3/2}}+\frac{1}{10^{3/2}}+\frac{1}{17^{3/2}}+\cdots\frac{1}{(1+n^2)^{3/2}}+\cdots\right)\right\},$$

due to the electrons in the line $Q''R''S''$; and

$$\frac{e^2}{a^2}\left\{\frac{1}{2^{3/2}}+2\left(\frac{1}{3^{3/2}}+\frac{1}{6^{3/2}}+\frac{1}{11^{3/2}}+\cdots\frac{1}{(2+n^2)^{3/2}}+\cdots\right)\right\}.$$

due to those along the line $Q'''R'''S'''$.

The first part is equal to

$$2{\cdot}03\,\frac{e^2}{a^2};$$

the second to

$$1{\cdot}01\,\frac{e^2}{a^2}.$$

Hence the force on P along P$''$P due to the other electrons is

$$3\cdot04\,\frac{e^2}{a^2}.$$

We now proceed to calculate the force on P due to the positive charges if the force between an electron and a positive charge E at a distance r is represented by

$$\frac{\mathrm{E}e}{r^2}\left(1-\frac{c}{r}\right).$$

The force on P along PP$''$ due to the positive charges will be

$$\frac{8\mathrm{E}e}{a^2}\left(\frac{1}{3^{3/2}}+\frac{1}{11^{3/2}}+\frac{1}{27^{3/2}}+\frac{1}{\{2+(2n+1)^2\}^{3/2}}+\dots\right)$$
$$-\frac{16\mathrm{E}ec}{a^3}\left(\frac{1}{3^2}+\frac{1}{11^2}+\frac{1}{27^2}+\dots\right)$$
$$=\frac{\mathrm{E}e}{a^2}\left(1\cdot89-\frac{c}{a}\,1\cdot95\right).$$

In order that the positive charges on the atoms should be numerically equal to the charges on the electrons, E must equal $4c$; so that the force due to the positive atoms is

$$\frac{e^2}{a^2}\left(7\cdot56-\frac{c}{a}\,7\cdot8\right).$$

Hence for equilibrium

$$3\cdot04\,\frac{e^2}{a^2}=\left(7\cdot56-\frac{c}{a}\,7\cdot8\right)\frac{c^2}{a^2};$$

so that

$$\frac{c}{a}=\cdot58.$$

Though this value of a would ensure the equilibrium of the system, it can be shown that the equilibrium is unstable. We might do this by obtaining the frequencies of the vibrations of the electrons about their position of equilibrium, but as the equilibrium proves to be unstable it is unnecessary to take this trouble, and we shall content ourselves with showing that the equilibrium is unstable for a particular displacement of the electrons.

The displacement we shall consider when P is displaced vertically upwards through a distance ρ, Q vertically downwards through the same distance, R vertically upwards. Thus the displacements of the electrons on the line P Q R..S are all of equal magnitude, but alternate displacements have opposite signs. The same is true for the electrons on the three other lines parallel to PQR; the displacements of electrons in the same vertical line are equal, but the displacement of any electron is of opposite sign to those of its three nearest neighbours on a horizontal plane.

The force due to the other electrons tending to increase ρ, the vertical displacement of P is

$$\frac{4\rho e^2}{a^3}\left(\frac{1}{1^3}+\frac{1}{3^3}+\frac{1}{5^3}+\dots\right)=\frac{\rho e^2}{a^3}(4\cdot207),$$

due to the electrons QRS,

plus $$\frac{2\rho e^2}{a^3}\left(\frac{1}{1^3}+2\left(\frac{1}{5^{3/2}}+\frac{1}{17^{3/2}}+\frac{1}{37^{3/2}}+\dots\right)\right)=\frac{\rho e^2}{a^3}(2\cdot408),$$

due to the electrons Q′R′S′,

plus $$\frac{4\rho e^2}{a^3}\left(\frac{1}{2^{3/2}}+\frac{1}{10^{3/2}}+\frac{1}{26^{3/2}}+\dots-3\left(\frac{1}{2^{5/2}}+\frac{1}{10^{5/2}}+\dots\right)\right)$$
$$=-\frac{\rho e^2}{a^3}\times\cdot568,$$

due to the electrons Q″R″S″,

plus $$\frac{2\rho e^2}{a^3}\left(\frac{1}{2^{3/2}}+2\left(\frac{1}{6^{3/2}}+\frac{1}{18^{3/2}}+\frac{1}{38^{3/2}}+\dots\right)-3\left(\frac{1}{2^{5/2}}+2\left(\frac{1}{6^{5/2}}\right.\right.\right.$$
$$\left.\left.\left.+\frac{1}{18^{5/2}}+\dots\right)\right)\right)=-\frac{\rho e^2}{a^3}\times\cdot1366,$$

due to the electrons Q‴R‴S‴.

Taking these together, the force tending to increase ρ is

$$\frac{\rho e^2}{a^3}\,5\cdot950.$$

Now consider the forces due to the positive atoms tending to diminish ρ; this is

$$16\rho\frac{Ee}{a^3}\left\{\frac{1}{3^{3/2}}+\frac{1}{11^{3/2}}+\frac{1}{27^{3/2}}+\dots\right.$$
$$\left.-3\left(\frac{1}{3^{5/2}}+\frac{1}{11^{5/2}}+\frac{1}{27^{5/2}}+\dots\right)\right\}$$
$$-32\rho\frac{Ee\,.\,c}{a^4}\left\{\frac{1}{3^2}+\frac{1}{11^2}+\frac{1}{27^2}+\dots-4\left(\frac{1}{3^3}+\frac{1}{11^3}+\dots\right)\right\}$$
$$=\rho\frac{Ee}{a^3}\left(\cdot53+\frac{c}{a}\cdot934\right).$$

Since $E=4e$ and $c/a=\cdot58$, this equals

$$\frac{\rho e^2}{a^3}\times4\cdot28.$$

Thus the force tending to increase the displacement is greater than that tending to diminish it, and so the equilibrium is unstable.

It follows from this result that the equilibrium of a long chain of carbon atoms alone must be unstable.

With atoms such as those of oxygen, which can have positive charges amounting to six units, a chain such as is shown in plan in fig. 6, where the electrons are at the corners of cubes placed so that each cube has an edge in common with its nearest neighbour, would satisfy the condition of having six electrons for each atom. An investigation similar to that just given shows, however, that the arrangement would be unstable. This is in accordance with experience, as long chains of oxygen are exceedingly unstable. A chain which I find to be just stable as far as the displacement of electrons is concerned is that where doubly charged atoms and electrons are arranged in the way shown in fig. 7.

Fig. 6.

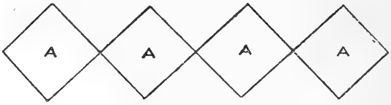
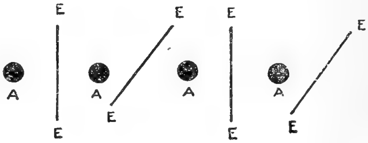


Fig. 7.



The atoms A are arranged at equal intervals along a straight line. The electrons are arranged in pairs, the line joining the constituents of a pair being at right angles to AA. Each pair is at right angles to its nearest neighbour. Each atom is thus at the centre of a regular tetrahedron formed by the electrons which are its next nearest neighbours. This arrangement is stable if the atoms are fixed; and the stability when the atoms are free to move can be insured by giving a suitable value to the force between two positively charged atoms.

If the radicle CH_2 be regarded as equivalent to an atom of a divalent element with two disposable electrons, then by the preceding result we might expect to get long chains of CH_2

radicle, though, as we have seen, we could not get them of carbon atoms. We know of many compounds which contain chains containing very large numbers of CH_2.

Summary.

A theory of the structure of solids is given based on the views as to the nature of the structure of the atom and the mechanism of chemical combination which I have given in previous papers in the Philosophical Magazine. Since the atom of a monovalent element has one disposable electron, that of a divalent element two, and so on, there must in a crystal of a monovalent element be such an arrangement of electrons and atoms that for each atom there is one electron, in a crystal of a divalent atom there must be two electrons for each atom, and so on. It is shown that this condition determines the crystallographic forms in which the various elements can crystallize, and leads to a conception of the structure of crystalline solids which allows us to calculate without further assumptions the values of certain physical constants such as the bulk modulus, the value of the critical frequency, and the dielectric constants. The values of these are calculated for elements of different valencies, and are found to agree closely with those found by experiment.

LXXXVIII. *Fluorescence and Photo-Chemistry.*
By R. W. Wood, *Johns Hopkins University* [*].

[Plate XVI.]

THOUGH it has been known for some time that many fluorescent solutions are bleached by the action of light, Perrin appears to have been the first to definitely associate fluorescence with chemical change and to regard the light emitted by fluorescent substances as due to the "flashes" of exploding molecules. Perrin showed that thin films of a solution of fluorescein were bleached at the spot on which the light was focussed by the sub-stage parabolic reflector used for the examination of colloidal particles under the microscope. He also examined other fluorescent substances and found that in all cases they were bleached with greater or less rapidity by the action of light.

[*] Communicated by the Author.

The experiments which I shall describe in the present paper were carried on in my summer laboratory at East Hampton in 1919 and 1920, and, though they were made with somewhat inadequate facilities, they appeared to establish certain points which were at variance with generally accepted views.

By operating with a very intense beam of light, obtained by concentrating sunlight with a short-focus lens 6 inches in diameter, sufficient quantities of the transformation products produced by the action of light on fluorescent solutions were obtained to make possible the examination of their optical and chemical properties. The time required to effect the change varies with the nature of the substance: eosine is completely changed in two or three minutes, while rhodamine in the same concentration requires several hours. Usually the decomposition of the fluorescent substance by the action of light yields a coloured non-fluorescent substance which is bleached by the further action of the light to a colourless solution. This makes it impossible to obtain the intermediate substance in a pure state; but, by choosing the proper concentration and stopping the illumination at the right moment, it was possible to obtain fairly satisfactory results.

The absorption spectra of the various compounds were photographed by mounting a prismatic cell of quartz filled with the solution in front of the slit of a quartz spectrograph, in which the prism was replaced with a plane grating, and illuminating the instrument with parallel rays of light. In this way we obtain the form of the absorption curve, as well as its location in the spectrum. The angle of the hollow prism was about 10°, and the thin edge (in a horizontal position) was brought into coincidence with the bottom of the slit. The refraction of the fluid prism was compensated by an opposed prism of quartz of about the same angle.

On Pl. XVI. will be found reproductions of some of the photographs. I have called the intermediate coloured substances photo-compounds, for want of a better name. Fluorescein (uranine), for example, which is lemon-yellow by transmitted light, is changed into a non-fluorescent compound (photo-fluorescein), which is orange-red, with an absorption band of a totally different form. The fluorescein band is very steep on the red side, sloping down gradually towards the region of shorter wave-lengths. The band shown by the photo-fluorescein, however, is more nearly symmetrical, sloping gradually in both directions. It is to this peculiarity that the red colour is due.

Continued illumination eventually bleaches the photo-compound.

Eosine behaves in a similar manner—the action of the light being much more rapid, however.

Rhodamine behaves in a very curious manner. A solution in water is gradually bleached by the action of the light without the formation of an intermediate coloured body, the absorption band fading away without change of form or position. In solution in methyl or ethyl alcohol, however, a strongly fluorescent intermediate body is formed, which emits a green fluorescence and exhibits an absorption band of totally different form from that shown by the rhodamine (which shows an orange-red fluorescence). The rhodamine absorption band has a double maximum, while the band of photo-rhodamine is single and shifted towards the region of shorter wave-lengths (see Pl. XVI.).

If the alcoholic solution of photo-rhodamine, which shows the green fluorescence, is evaporated, and the residue dissolved in water, the solution shows the same green fluorescence—a circumstance which is interesting in connexion with the fact that the photo-rhodamine cannot be formed by the action of light on an aqueous solution. It seems probable that in this case the photo-compound may be formed also as an intermediate product, but its rate of decomposition is as great as that of the rhodamine. It is clear that to obtain a recognizable amount of an intermediate body it must be more stable under the action of the light than the original substance; otherwise it will disappear as rapidly as it is formed.

It was thought that the rhodamine might be a mixture of two substances—one having a single absorption band at 5500, the other with a band at 5200, the double band actually photographed being the superposition of the two. If this were the case the first substance would probably yield a red fluorescence, the second a green fluorescence; and if the former were decomposed more rapidly by the action of the light we should have observed change in the colour of the fluorescent light without the intervention of an intermediate body: in other words, the green fluorescence would be present initially, but masked by the orange-red fluorescence. This point was tested by examining the fluorescent light of two solutions simultaneously with a grating—one a solution of rhodamine, the other a solution of photo-rhodamine formed by the action of light on a solution of rhodamine of similar concentration. In this way the fluorescent light was spread out into a spectrum and the possible masking effect was eliminated. It was found that the green fluorescence was enormously stronger in the case of the photo-rhodamine than in the case of the original solution. This makes it seem certain that we have an intermediate coloured body, which is fluorescent. Perrin has recorded similar results.

A number of other fluorescent substances were examined, with the following results :—

Phloxine : Bleached by the action of light, the absorption band remaining in its original position and gradually fading away.

Resorufine : Similar to phloxine.

Acridine Orange : Solution yellow by transmitted light, becomes reddish after long illumination, with broadened absorption band. Much like fluorescein.

Napthaline Red : Alcoholic solution shows orange fluorescence. Bleached by illumination, with no trace of other coloured compound. Solution in hot water : Illumination causes the precipitation of a fine suspension which gives a bluish colour by transmitted light. The precipitate is soluble in alcohol and shows fluorescence similar to that of the alcoholic solution of the original substance, but less bright.

Influence of Temperature on Fluorescence.

Perrin states in his paper (*Annales de Physique*, 1918) that the intensity of the fluorescent light is independent of temperature, and draws a comparison between fluorescence and radio-activity.

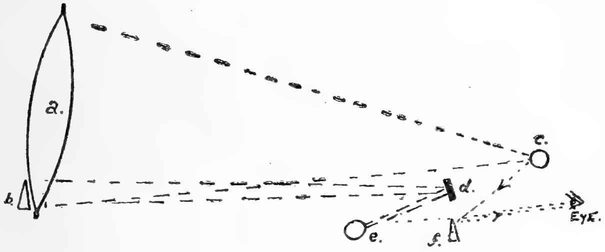
I have found, however, that rhodamine is almost non-fluorescent in a water solution at 100°. The observation was first made in the case of a small tube containing about 1 c.c. of the solution, illuminated with sunlight focussed by the large lens. The solution was raised to the boiling-point in about a minute and the fluorescence disappeared, reappearing if the solution was cooled. Fluorescein appeared to be slightly brighter at zero than at room-temperature, and slightly less at 100°. Eosine showed no temperature effect. On account of the peculiar temperature effect in the case of rhodamine, it was necessary to keep the solutions cool by a water jacket during the transformation experiments recorded in the previous section.

Intensity Relation between Fluorescent and Exciting Light.

It has been pretty well established that the intensity of the fluorescent light is proportional to the intensity of the exciting light. Knoblauch reduced the intensity of his exciting beam to 1/6400 by means of dark glass, and found that the relation held. As his maximum intensity fell far short of the intensity at the focus of my lens (which was roughly 1400 times the intensity of normal sunlight, and as it was very essential for the interpretation of the results of certain experiments about to be described to be sure that the relation held for the very high intensities used, the following very simple and instructive experiment was made.

The theory of the experiment will be made clear by fig. 1. The 6-inch lens *a* was illuminated by sunlight, and a small prism *b* of about 10° was mounted near one edge of it. The area of this prism which was exposed was 4 per cent. of the area of the lens not covered by the prism. This ratio of areas was chosen for reasons which will appear presently. The powerful beam concentrated by the lens illuminated the small bottle *c*, which was filled with a solution of fluorescein. The beam deflected by the prism was reflected by the silvered mirror *d* and concentrated on the bottle *e*, which also contained fluorescein. The ratio of the illuminating intensities was thus 4 : 100. If the fluorescent ratios were in the same ratio, then the image of the fluorescent spot on bottle *c* seen reflected in a *single* surface of glass (4 per cent. reflexion coeff.) should have the same intensity as the fluorescent spot on bottle *e* viewed directly. The reflexion was taken from the surface of a small prism *f*, the opposite surface having been painted with black paint to prevent reflexion.

Fig. 1.



As this prism had a razor-edge, it was possible by holding the eye and prism in suitable positions to bring the two images together with a sharp line of separation between them. This line was found to be practically invisible, showing equality of the intensities and proving that the law holds up to the very high intensities used. The lens was then stopped down to 1/600,000 of its full aperture by means of a sheet of black paper with a small pin-hole in it. Even with this enormous reduction in the fluorescent spot on the bottle *c* the fluorescence was distinctly visible, which shows us that we can increase the intensity of a beam of light, which is sufficiently intense to cause the decomposition of the fluorescein molecules, six hundred thousandfold without causing the instantaneous destruction of all of them—in fact, an exposure of ten or fifteen minutes to the intense beam is necessary before the transformation is complete.

Perrin's theory is that the intensity of the fluorescent light emitted by a single molecule is independent of the intensity of the exciting light, and that the increase in the intensity of the total emitted light is due merely to the circumstance that more molecules are being destroyed (or transformed) per unit of time in the case of intense illumination. In support of this, we have the circumstance that sooner or later the fluorescent solutions are bleached by the action of the light. But this is also true of a large number of non-fluorescent solutions of organic colouring-matters.

We can make the alternative hypothesis that all of the molecules in the solution fluoresce to an equal degree, and that as the intensity of the exciting light increases the amplitude of the fluorescent radiation emitted by each molecule increases to a corresponding degree. While this is going on the solution is gradually undergoing decomposition by the action of the light, as in the case of a non-fluorescent solution. It seems extremely desirable to devise experiments which will enable us to choose the more probable of the two hypotheses. Two such experiments suggested themselves.

Are the Molecules Fluorescent only at the Moment of Breakdown?

It would appear as if some light might be thrown on the two alternative hypotheses mentioned above if we can prevent fluorescence and still allow light to act on the medium. There are two ways in which this can be done. As has been already stated, the fluorescence of an aqueous solution of rhodamine nearly ceases at 100°. Moreover, fluorescence ceases if the concentration becomes too great, due to what Perrin calls protective action.

If, now, it be found that preventing the fluorescence by these means prevents the bleaching of the solution by the action of light, it will be a strong argument for the theory of Perrin. On the other hand, if it be found that bleaching proceeds at the same rate as before, we shall have grounds for suspecting that the fluorescence is not directly connected with the breakdown of the molecule.

Both of these experiments have been tried. A strong solution of eosine was made which showed no trace of fluorescence, even in concentrated sunlight. A carefully measured amount of this solution ($\frac{1}{4}$ c.c.) was introduced into a small cylindrical flat-bottomed bottle and illuminated by a vertical beam of sunlight concentrated by the six-inch lens for half an hour. The bottle was kept cool by immersion in a beaker of water during the experiment. A similar amount of the strong solution diluted with 5 c.c. of water was subjected to a similar treatment for the same length of time, fluorescing brilliantly throughout the experiment. The contents of the first tube were now diluted to the same volume, and the contents of the two tubes compared. The concentrated solution had suffered no change from the action of the light, while the diluted solution was largely made up of the photo-eosine, as was shown by its red colour and feebler fluorescence.

This indicates that proximity of the molecules protects the solution against decomposition as well as against fluorescence, and argues in favour of the theory that the decomposition results from the fluorescence.

The experiment of inhibiting the fluorescence of rhodamine by raising it to a temperature of 100° was next tried. Two small tubes were prepared, of equal size, and equal amounts of a dilute solution of rhodamine introduced into them. They were then sealed in a flame as close as possible to the surface of the solution. One tube was mounted in a beaker of cold water close to the wall, the other in a beaker of water kept boiling by a Bunsen burner. Both were illuminated simultaneously by sunlight concentrated by two six-inch lenses, which formed images of the sun of a diameter about half that of the tubes. In this experiment the conditions were exactly the same, except that one tube was at a higher temperature than the other. The fluorescence of the cold solution was about twenty times as bright as that of the hot solution, yet decomposition proceeded at practically the same rate in the two cases. At the end of half an hour the colour had been considerably reduced, but no difference could be detected, except that the fluorescence of the high-temperature tube, after it had been cooled off, was slightly greenish in colour, while that of the other was orange-yellow as at the beginning of the experiment, only much less bright owing to the partial decomposition.

This was a rather disappointing result from the point of view of confirming Perrin's theory. A control experiment showed that the rhodamine solution was not bleached by an hour's heating in a sealed tube immersed in a beaker of boiling water.

Attention is drawn to the fact that not all samples of rhodamine are sensitive to temperature. I have, in all, about a dozen different rhodamines of which only two show the very marked loss of fluorescent power at 100°.

Function of the Intensity of the Exciting Light.

A very remarkable relation between the rate of breakdown of eosine and the intensity of the exciting light was discovered, which has probably a very direct bearing on Perrin's theory. Stating it in simple form, we may say that high intensities acting for a short time produce a greater amount of decomposition than low intensities acting for a long time, the time being increased in proportion to the reduction of the intensity, of course. This means that the change is not proportional to the amount of energy extracted from the incident light—a rather surprising result, and one at variance with the Bunsen-Roscoe law.

The experiment was made in the following way:—Two circular cells were made, each six inches in diameter and $\frac{1}{4}$ inch in thickness, by cementing glass disks to brass rings. Each cell was filled with a solution of eosine of the same concentration. One cell was exposed normally to direct sunlight, the other to sunlight concentrated by a six-inch lens. The solar image was formed near the bottom of the cell, so that the convection would be as complete as possible. In each case the same amount of light is passed through the cell, and through the same thickness of solution ($\frac{1}{4}$ inch). The only difference is that in one case it is spread uniformly over the whole area of the cell, and in the other case it is concentrated on an area of very small size.

Variations in the intensity of the sunlight during the experiment make no difference, as both cells are affected by them to the same degree.

After an exposure of three hours it was found that the cell receiving the concentrated illumination showed a much greater change than the one exposed to normal sunlight. Its fluorescence was less, and the colour of the transmitted light much redder (due to the formation of a greater quantity of photo-eosine).

The gain in the action by increasing the intensity is probably even more marked than is shown by this experiment. To perform the experiment in an ideal manner a given amount of the solution should pass only once through the concentrated light-beam. As a matter of fact, there is a strong convection current upward, due to the heating of the liquid at the focus, and the solution which has passed through the beam and been partially decomposed mixes with the fresh solution and dilutes it, so to speak. This will make the increased action due to high intensity of the light less marked than it would be if the solution could be kept at rest, and the solar image moved over every portion of the cell in a perfectly uniform manner, so that each surface element would receive equal exposure.

This relation between the intensity of the light and the rate of change is evidently extremely important, and it is being subjected to a careful quantitative investigation at the present time in collaboration with Mr. Subkow, one of my students.

Unstable dyes, which are non-fluorescent, do not behave in this way, the bleaching in the two cells being equal in amount.

We now have at our disposal a mirror of 32 inches aperture and 18 inches focus, with which platinum-foil can be instantly melted by concentrated sunlight. With this mirror the photo compounds can be made in quantity sufficient for chemical examination.

LXXXIX. *Note on a possible Relationship between the Focal Length of Microscope Objectives, and the number of Fringes seen in Convergent Polarized Light.* *By* F. Ian G. Rawlins *.

In connexion with a statement by Groth ('Optical Properties of Crystals,' Chapman & Hall, 1910), to the effect that the number of interference fringes seen in crystals by means of a microscope in convergent polarized light is a function of the focal length of the objectives used, it was considered of interest to investigate this—in as simple a way as possible—with a view to determining whether such relationship was capable of exact mathematical expression: more especially since inquiry into the literature of the subject failed to show that this aspect of the question had received attention.

Three crystals were available for trial (quartz, tourmaline, and mica), the approximate thicknesses being 5, 4, and 1 mm. respectively. It is clearly necessary to have sections of unusual thickness, otherwise a sufficient number of observations cannot be made. Daylight was used together with a red gelatine filter. The objectives were ordinary achromatic lenses, and the figures were viewed by means of a supplementary Becké lens above the eyepiece.

The following data were obtained:—

Quartz.		Tourmaline.		Mica.	
Focal Length of Objective in mm. =F.	No. of Rings =N.	Focal Length of Objective in mm. =F.	No. of Rings =N.	Focal Length of Objective in mm. =F.	No. of Rings =N.
32	0	32	9	16	1
22	2	22	2	8	4
16	4	16	4	4	7
8	8	8	11		
4	11	4	16		

These results are plotted on the accompanying graph (dotted-line curves), from which it will be seen that a fairly smooth curve can be drawn through the points. Plotting log F against log N was a failure in so far that a straight line was not forthcoming.

A trial was then made by taking for variables $\log_e F$ and N, and the points shown in solid lines were obtained. It is apparent that straight lines can be drawn through these

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* Communicated by the Author.

with considerable accuracy. This at once suggests an exponential equation of the form

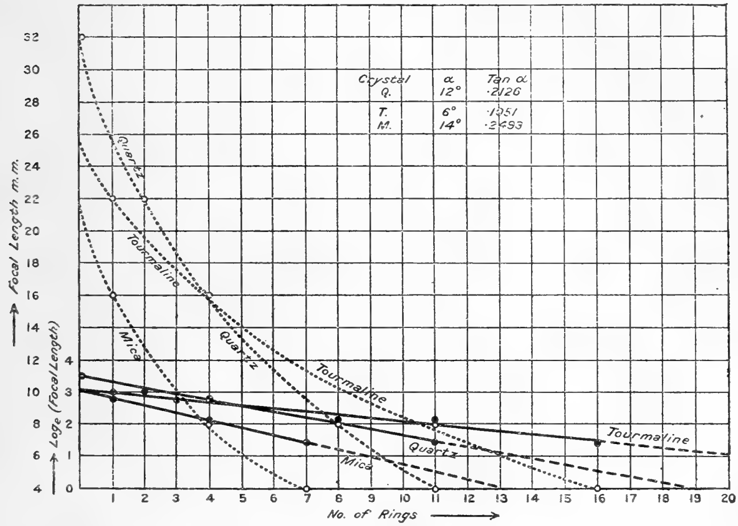
$$\frac{dF}{dN} = -AF \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(where A is a constant), or

$$\int \frac{dF}{F} = -\int A \, . \, dN, \quad . \quad . \quad . \quad . \quad (2)$$

from which we obtain

$F = F_0 e^{-AN}$ as the equation required.



Measurement of the angle made with the axis of N gives the following values for A :—

Quartz	·2126
Tourmaline	·1051
Mica.....................	·2493

A is necessarily a mere number, and it is of great interest to speculate as to its nature. Since monochromatic light was not available, it is evidently useless to attempt to identify A with any function of the index of refraction or bi-refringence of the crystals used.

If we invert equation (1), we obtain the result that the rate of decrease of the number of fringes with focal length is proportional to the reciprocal of the focal length itself.

These results, though very elementary, seem to show that another case in nature has been found to add to the list of known phenomena following a logarithmic law of decay.

XC. *On Products of Legendre Functions.* *By* J. W. Nicholson, *F.R.S., Fellow of Balliol College, Oxford* *.

THE fact that it is possible to express the product of the two functions $P_n(\mu)$, $P_m(\mu)$ as a series of functions of the type $P_r(\mu)$ was discovered independently by Couch Adams and Ferrers many years ago. Apart from a paper by Sir William Niven, the subject of these products, which can be developed in a manner of some significance for applied mathematics, does not appear to have attracted the attention which it deserves. Niven's paper made a notable advance, being essentially more general in its scope than the intuitive method of the earlier investigators—afterwards arranged more concisely by Todhunter. But no author has considered the equally interesting and important products in which functions of the type $Q_n(\mu)$ appear, though these can be included in an investigation by a method which is, after Poincaré, now familiar in the theory of differential equations. An outline of this investigation, with some of the more important properties of the functions, is our immediate object.

Let an accent denote a differentiation with respect to μ, and let P stand for $P_n(\mu)$ or $Q_n(\mu)$, and Q for $P_m(\mu)$, $Q_m(\mu)$. For convenience, we write also $M=m(m+1)$, $N=n(n+1)$. Then

$$(1-\mu^2)P''=2\mu P'-NP,$$

$$(1-\mu^2)Q''=2\mu Q'-MQ.$$

We first form the linear differential equation of the fourth order satisfied by PQ. Its general solution must be

$$A\,P_nP_m+B\,P_nQ_m+C\,P_mQ_n+D\,Q_mQ_n,$$

where A, B, C, D are constants, and from its solution in the form of series we can derive the four typical products.

If

$$y=PQ,$$

we have

$$y'=\frac{dy}{d\mu}=PQ'+QP',$$

$$y''=2P'Q'+PQ''+QP''$$

$$=2P'Q'+\frac{P}{1-\mu^2}(2\mu Q'-MQ)+\frac{Q}{1-\mu^2}(2\mu P'-NP),$$

whence

$$(1-\mu^2)y''-2\mu y'+(M+N)y=2P'Q'(1-\mu^2).$$

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* Communicated by the Author.

The operation

$$(1-\mu^2)\frac{d^2}{d\mu^2}-2\mu\frac{d}{d\mu}\equiv\frac{d}{d\mu}(1-\mu^2)\frac{d}{d\mu}$$

may be conveniently called D, so that

$$(\mathrm{D}+\mathrm{M}+\mathrm{N})y=2\mathrm{P}'\mathrm{Q}'(1-\mu^2).$$

Accordingly

$$\begin{aligned}(1-\mu^2)\frac{d}{d\mu}\,.\,(\mathrm{D}+\mathrm{M}+\mathrm{N})y&=(1-\mu^2)\frac{d}{d\mu}\left\{2\mathrm{P}'\mathrm{Q}'(1-\mu^2)\right\}\\ &=-4\mu(1-\mu^2)\mathrm{P}'\mathrm{Q}'+2(1-\mu^2)^2(\mathrm{P}''\mathrm{Q}'+\mathrm{Q}''\mathrm{P}')\\ &=-4\mu(1-\mu^2)\mathrm{P}'\mathrm{Q}'+2(1-\mu^2)\mathrm{Q}'(2\mu\mathrm{P}'-\mathrm{NP})\\ &\qquad+2(1-\mu^2)\mathrm{P}'(2\mu\mathrm{Q}'-\mathrm{MQ})\\ &=\quad 4\mu(1-\mu^2)\mathrm{P}'\mathrm{Q}'-2(\mathrm{MP}'\mathrm{Q}+\mathrm{NPQ}')(1-\mu^2).\end{aligned}$$

Substituting for P′Q′, this may be reduced to

$$\begin{aligned}(1-\mu^2)\frac{d}{d\mu}\,.\,(\mathrm{D}+\mathrm{M}+\mathrm{N})y-2\mu(\mathrm{D}+\mathrm{M}+\mathrm{N})y\\ =-2(1-\mu^2)(\mathrm{MP}'\mathrm{Q}+\mathrm{NPQ}')\end{aligned}$$

Differentiating again with respect to μ,

$$\begin{aligned}\mathrm{D}(\mathrm{D}+\mathrm{M}+\mathrm{N})y-2\frac{d}{d\mu}\,.\,\mu(\mathrm{D}+\mathrm{M}+\mathrm{N})y&\\ =4\mu(\mathrm{MP}'\mathrm{Q}+\mathrm{NPQ}')-2(1-\mu^2)(\mathrm{M}+\mathrm{N})\mathrm{P}'\mathrm{Q}'&\\ -2(1-\mu^2)(\mathrm{MP}''\mathrm{Q}+\mathrm{NPQ}'')&\\ =4\mu(\mathrm{MP}'\mathrm{Q}+\mathrm{NPQ}')-2(1-\mu^2)(\mathrm{M}+\mathrm{N})\mathrm{P}'\mathrm{Q}'&\\ -2\mathrm{MQ}(2\mu\mathrm{P}'-\mathrm{NP})-2\mathrm{NP}(2\mu\mathrm{Q}'-\mathrm{MQ})&\\ =4\mathrm{MN}y-2(1-\mu^2)(\mathrm{M}+\mathrm{N})\mathrm{P}'\mathrm{Q}'&\end{aligned}$$

on reduction. Again substituting for P′Q′,

$$\begin{aligned}\mathrm{D}(\mathrm{D}+\mathrm{M}+\mathrm{N})y-2\frac{d}{d\mu}\,.\,\mu(\mathrm{D}+\mathrm{M}+\mathrm{N})y-4\mathrm{MN}y\\ +(\mathrm{M}+\mathrm{N})(\mathrm{D}+\mathrm{M}+\mathrm{N})y=0,\end{aligned}$$

which we may write in the form

$$(\mathrm{D}+\mathrm{M}+\mathrm{N})^2y=2\frac{d}{d\mu}\,.\,\mu(\mathrm{D}+\mathrm{M}+\mathrm{N})y+4\mathrm{MN}y.$$

This is the required equation of the fourth order. In this form, it is much more convenient than when expanded in full.

Solution in Series of P *Functions.*

A series solution in powers of μ cannot be obtained in a simple form, but one solution in zonal harmonics of integral order is readily possible, as we know from Adams' expression for $P_n(\mu)P_m(\mu)$, and it must have a simple general term. We may anticipate the existence of other series solutions of this type representing such solutions as

$$y = P_n(\mu)\,Q_m(\mu).$$

Write

$$y = \Sigma_\alpha^\beta a_r P_r(\mu),$$

the summation being for integral values of r, and the limits α and β being at present unknown.

Then

$$Dy \equiv \frac{d}{d\mu} \,.\, 1-\mu^2 \,.\, \frac{dy}{d\mu} = -\Sigma_\alpha^\beta r(r+1) a_r P_r(\mu).$$

Write

$$R \equiv r(r+1),$$

and we find that

$$\Sigma_\alpha^\beta \left\{ (M+N-R)^2 - 4MN \right\} a_r P_r(\mu)$$
$$= 2\frac{d}{d\mu} \,.\, \mu\, \Sigma_\alpha^\beta (M+N-R) a_r P_r(\mu).$$

Quoting the recurrence formulæ,

$$(2r+1)\mu P_r = (r+1)P_{r+1} + rP_{r-1},$$

$$(2r+1)P_r = \frac{dP_{r+1}}{d\mu} - \frac{dP_{r-1}}{d\mu},$$

we may change this to the form,

$$\Sigma_\alpha^\beta \left\{ (M+N-R)^2 - 4MN \right\} \frac{a_r}{2r+1} \left\{ \frac{dP_{r+1}}{d\mu} - \frac{dP_{r-1}}{d\mu} \right\}$$

$$= 2\frac{d}{d\mu} \Sigma_\alpha^\beta (M+N-R) \frac{a_r}{2r+1} (r+1 \,.\, P_{r+1} + rP_{r-1})$$

$$= 2\,\Sigma_\alpha^\beta (M+N-R) \frac{a_r}{2r+1} \left\{ r+1 \,.\, \frac{dP_{r+1}}{d\mu} + r\frac{dP_{r-1}}{d\mu} \right\},$$

which must be satisfied identically for all values of μ. In another form,

$$\Sigma_{\alpha}^{\beta}\frac{a_r}{2r+1}\cdot\frac{dP_{r+1}}{d\mu}\left\{(M+N-R)^2-4MN-2(r+1)(M+N-R)\right\}$$

$$=\Sigma_{\alpha}^{\beta}\frac{a_r}{2r+1}\,\frac{dP_{r-1}}{d\mu}\left\{(M+N-R)^2-4MN+2r(M+N-R)\right\}.$$

Clearly the values of r are α, $\alpha+2$, ..., alternate functions being missing. The series on the right contains a term of lower index than any on the left unless its coefficient is zero. The indicial equation, for an *ascending* series of P functions in which the order increases by two is therefore

$$(M+N-R)^2-4MN+2r(M+N-R)=0,$$

where $r=\alpha$. This determines the possible values of α.

The equation is a quartic, and becomes, in full,

$$(m^2+m+n^2+n-\alpha^2-\alpha)(m^2+m+n^2+n-\alpha^2+\alpha)$$
$$=4(m^2+m)(n^2+n),$$

which can be reduced to

$$\alpha^4-\alpha^2(1+2m^2+2n^2+2m+2n)+(m-n)^2(m+n+1)^2=0,$$

whose roots are

$$\alpha=m-n,\quad n-m,\quad m+n+1,\quad -(m+n+1).$$

Whether m or n be the greater, two ascending series beginning with a function P of positive order are available. If we confine ourselves to integral values of m and n, which are the cases of practical value, we select $\alpha=m+n+1$ and $\alpha=m-n$ or $n-m$, whichever be positive.

For a *descending* series, in which the order of the P functions decreases by two, we choose β to satisfy, when $r=\beta$,

$$(M+N-R)^2-4MN-2(r+1)(M+N-R)=0$$

—the extra term being on the other side of the identical relation.

This is the quartic

$$(m^2+m+n^2+n-\beta^2-\beta)(m^2+m+n^2+n-\beta^2-3\beta-2)$$
$$=4(m^2+m)(n^2+n)$$

which is more troublesome, but which factorizes ultimately to

$$(\beta+m+n+2)(\beta-m-n)(\beta+m-n+1)(\beta-m+n+1)=0,$$

and the possible values of β are

$$-(m+n+2), \quad m+n, \quad m-n-1, \quad n-m-1.$$

The second clearly will lead to Adams' formula.

The Ascending Series.

We may now write the identical relation in the form

$$\sum_{\alpha}^{\beta}(r+m+n+2)(r-m-n)(r+m-n+1)(r-m+n+1) \times \frac{a_r}{2r+1}\frac{dP_{r+1}}{d\mu}$$

$$=\sum_{\alpha}^{\beta}(r+m+n+1)(r-m-n-1)(r+m-n)(r+n-m) \times \frac{a_r}{2r+1}\frac{dP_{r-1}}{d\mu},$$

or its equivalent,

$$\sum_{\alpha}^{\beta}(r+m+n+2)(r-m-n)(r+m-n+1)(r-m+n+1) \times \frac{a_r}{2r+1}\frac{dP_{r+1}}{d\mu}$$

$$=\sum_{\alpha}^{\beta}(r+m+n+3)(r-m-n+1)(r+m-n+2) \times (r+n-m+2)\frac{a_{r+2}}{2r+5}\frac{dP_{r+1}}{d\mu}$$

$$+(\alpha+m+n+1)(\alpha-m-n-1)(\alpha+m-n)(\alpha+n-m) \times \frac{a_\alpha}{2\alpha+1}\frac{dP_{\alpha-1}}{d\mu}.$$

The last term, not under the sign of summation, vanishes if α is chosen appropriately, as above, for an ascending series. We then deduce, for any value of r equal to or greater than α,

$$\frac{a_{r+2}}{a_r}=\frac{2r+5}{2r+1}\cdot\frac{r+m+n+2}{r+m+n+3}\cdot\frac{r-m-n}{r-m-n+1} \cdot\frac{r+m-n+1}{r+m-n+2}\cdot\frac{r-m+n+1}{r-m+n+2},$$

and the corresponding solution

$$y = a_\alpha \left\{ P_\alpha(\mu) + \frac{a_{\alpha+2}}{a_\alpha} P_{\alpha+2}(\mu) + \frac{a_{\alpha+4}}{a_{\alpha+2}} \cdot \frac{a_{\alpha+2}}{a_\alpha} P_{\alpha+4}(\mu) + \ldots \right\},$$

where a_α is arbitrary.

For the first series, write $\alpha = m+n+1$, and we find the solution

$$y = P_{m+n+1} + \frac{1}{2} \cdot \frac{2m+2 \,.\, 2n+2}{2m+3 \,.\, 2n+3} \cdot \frac{2m+2n+3}{2m+2n+4} \cdot \frac{2m+2n+7}{2m+2n+3} \times P_{m+n+3}$$

$$+ \frac{1 \,.\, 3}{2 \,.\, 4} \cdot \frac{2m+2 \,.\, 2m+4 \,.\, 2n+2 \,.\, 2n+4}{2m+3 \,.\, 2m+5 \,.\, 2n+3 \,.\, 2n+5}$$

$$\cdot \frac{2m+2n+3 \,.\, 2m+2n+5}{2m+2n+4 \,.\, 2m+2n+6} \cdot \frac{2m+2n+7 \,.\, 2m+2n+11}{2m+2n+3 \,.\, 2m+2n+7} \times P_{m+n+5} + \ldots ;$$

multiplying by a constant, we may take instead the form

$$y = \sum_{r=0}^{\infty} 2^{-2r} \cdot \frac{\Gamma(m+r+1)\,\Gamma(n+r+1)\,\Gamma(m+n+r+\frac{3}{2})}{\Gamma(m+r+\frac{3}{2})\,\Gamma(n+r+\frac{3}{2})\,\Gamma(m+n+r+2)}$$

$$\cdot \frac{2r\,!}{(r\,!)^2} (2m+2n+4r+3)\, P_{m+n+1+2r},$$

which may be called *Series A*, and to which we shall return later.

For the second ascending series, we suppose $m > n$. Then $\alpha = m-n$, and the series becomes

$$y = P_{m-n} + \frac{1}{2} \left\{ \frac{2m+2}{2m+3} \cdot \frac{2n}{2n-1} \cdot \frac{2m-2n+1}{2m-2n+2} \right\} \frac{2m-2n+5}{2m-2n+1} \times P_{m-n+2}$$

$$+ \frac{1 \,.\, 3}{2 \,.\, 4} \left\{ \frac{2m+2 \,.\, 2m+4}{2m+3 \,.\, 2m+5} \cdot \frac{2n \,.\, 2n-2}{2n-1 \,.\, 2n-3} \right.$$

$$\left. \cdot \frac{2m-2n+1 \,.\, 2m-2n+3}{2m-2n+2 \,.\, 2m-2n+4} \right\} \frac{2m-2n+9}{2m-2n+1} P_{m-n+4} + \ldots .$$

We notice that it terminates with the term in P_{m+n}, so that it must be a multiple of Adams' series, and in fact can be arranged equally as a descending series. We may call it *Series B*.

The Descending Series.

The identical relations can also be written

$$(\beta+m+n+2)(\beta-m-n)(\beta+m-n+1)(\beta-m+n+1)$$
$$\times\frac{\alpha_\beta}{2\beta+1}\frac{d\mathrm{P}_{\beta+1}}{d\mu}$$
$$+\sum_\alpha^{\beta-2}(r+m+n+2)(r-m-n)(r+m-n+1)(r-m+n+1)$$
$$\times\frac{a_r}{2r+1}\frac{d\mathrm{P}_{r+1}}{d\mu}$$
$$=\sum_\alpha^{\beta}(r+m+n+1)(r-m-n-1)(r+m-n)(r+n-m)$$
$$\times\frac{a_r}{2r+1}\frac{d\mathrm{P}_{r-1}}{d\mu},$$

where the first term vanishes if β is chosen suitably. This is equivalent to

$$\sum^{\beta}(r+m+n)(r-m-n-2)(r+m-n-1)(r-m+n-1)$$
$$\times\frac{a_{r-2}}{2r-3}\frac{d\mathrm{P}_{r-1}}{d\mu}$$
$$=\sum^{\beta}(r+m+n+1)(r-m-n-1)(r+m-n)(r+n-m)$$
$$\times\frac{a_r}{2r+1}\frac{d\mathrm{P}_{r-1}}{d\mu}.$$

The last term, r being an integer like m, n, involves $\frac{d\mathrm{P}_1}{d\mu}$ or zero, thus defining α. We find

$$\frac{a_{r-2}}{a_r}=\frac{2r-3}{2r+1}\cdot\frac{r+m+n+1}{r+m+n}\,\frac{r-m-n-1}{r-m-n-2}\,\frac{r+m-n}{r+m-n-1}$$
$$\times\frac{r+n-m}{r+n-m-1},$$

and the series is, a_β being arbitrary, proportional to

$$y=\mathrm{P}_\beta(\mu)+\frac{a_{\beta-2}}{a_\beta}\mathrm{P}_{\beta-2}(\mu)+\frac{a_{\beta-4}}{a_{\beta-2}}\cdot\frac{a_{\beta-2}}{a_\beta}\mathrm{P}_{\beta-4}(\mu)+\ldots.$$

Taking $\beta=m+n$, we have

$$y=\mathrm{P}_{m+n}(\mu)+\frac{1}{2}\cdot\frac{2m\,.\,2n}{2m-1\;2n-1}\cdot\frac{2m+2n+1}{2m+2n}\cdot\frac{2m+2n-3}{2m+2n+1}$$
$$\times\mathrm{P}_{m+n-2}(\mu)+\ldots.$$

This is essentially Adams' theorem, and the same as *Series B*. Since $P_m(\mu)$, $P_n(\mu)$ are polynomials of degrees m, n respectively, and the Q functions are infinite series, we may, by equating coefficients of μ^{m+n}, derive at once

$$P_n(\mu)P_m(\mu)=\frac{2n\,!\;2m\,!\;(m+n\,!)^2}{(m\,!\;n\,!)^2\,(2m+2n\,!)}\,y,$$

giving the complete expansion of P_mP_n, and thence the value of the integral

$$\int_{-1}^{1}P_mP_nP_r\,d\mu$$

for all integer values of m, n, and r. The results are known.

The Second Descending Series.

The second series, if $m>n+1$, has the indicial equation

$$\beta=m-n-1$$

and the form defined by

$$y=P_\beta(\mu)+\frac{a_{\beta-2}}{a_\beta}P_{\beta-2}(\mu)+\ \ldots\ .$$

with $\beta=m-n-1$.

Now again,

$$\frac{a_{r-2}}{a_r}=\frac{2r-3}{2r+1}\cdot\frac{r+m+n+1}{r+m+n}\,\frac{r-m-n-1}{r-m-n-2}\cdot\frac{r+m-n}{r+m-n-1}\cdot\frac{r+n-m}{r+n-m-1},$$

and the series becomes

$$y=P_{m-n-1}+\frac{1}{2}\cdot\frac{2m}{2m-1}\cdot\frac{2n+2}{2n+3}\cdot\frac{2m-2n-1}{2m-2n-2}\cdot\frac{2m-2n-5}{2m-2n-1}\times P_{m-n-}$$

$$+\frac{1\,.\,3}{2\,.\,4}\cdot\frac{2m\,.\,2m-2}{2m-1\,.\,2m-3}\cdot\frac{2n+2\,.\,2n+4}{2n+3\,.\,2n+5}\cdot\frac{2m-2n-1\,.\,2m-2n-3}{2m-2n-2\,.\,2m-2n-4}\cdot\frac{2m-2n-9}{2m-2n-1}P_{m-n-5}+\ \ldots\ .$$

We shall denote this as *Series C.* It stops just before the P's are of negative order.

This series we must proceed to identify. From the order in μ of the functions P which occur, it cannot involve $P_m P_n$, in which they are of orders $m+n$, $m+n-2$, ... or $Q_m Q_n$, in which they are clearly of orders $m+n+2$, $m+n$, ... It is therefore a linear combination of $P_m Q_n$ and $P_n Q_m$, and since it is a *terminating* series, it must be of the type

$$A(P_m Q_n - P_n Q_m).$$

For this is the only such type which is polynomial. We know from Christoffel's formula that

$$Q_n = \tfrac{1}{2} P_n \log \frac{1+\mu}{1-\mu} + \lambda_{n-1},$$

where λ_n is a polynomial in μ, of degree $n-1$. Thus

$$\begin{aligned} P_m Q_n - P_n Q_m & \\ &= \frac{P_m P_n}{2} \log \frac{1+\mu}{1-\mu} + \lambda_{n-1} P_m - \frac{P_n P_m}{2} \log \frac{1+\mu}{1-\mu} - \lambda_{m-1} P_n \\ &= P_m \lambda_{n-1} - P_n \lambda_{m-1}, \end{aligned}$$

which is a polynomial whose degree cannot exceed $n+m-1$. No other such polynomial can be constructed, all other combinations being logarithmic.

Now when $n=0, 1, 2, \ldots$ we find that the series y becomes

$$\begin{aligned} y_0 = P_{m-1} &+ \frac{1}{3} \cdot \frac{2m \,.\, 2m-5}{2m-2 \,.\, 2m-1} P_{m-3} \\ &+ \frac{1}{5} \cdot \frac{2m \,.\, 2m-9}{2m-4 \,.\, 2m-1} P_{m-5} + \ldots . \end{aligned}$$

$$\begin{aligned} y_1 = P_{m-2} &+ \frac{1 \,.\, 4}{2 \,.\, 5} \cdot \frac{2m \,.\, 2m-7}{2m-4 \,.\, 2m-1} P_{m-4} \\ &+ \frac{1 \,.\, 3 \,.\, 6}{2 \,.\, 5 \,.\, 7} \cdot \frac{2m \,.\, 2m-2 \,.\, 2m-5 \,.\, 2m-11}{2m-1 \,.\, 2m-3 \,.\, 2m-4 \,.\, 2m-6} P_{m-6} + \ldots , \end{aligned}$$

$$y_2 = P_{m-3} + \frac{1 \,.\, 6}{2 \,.\, 7} \cdot \frac{2m \,.\, 2m-9}{2m-6 \,.\, 2m-1} P_{m-5} + \ldots .$$

These may be compared with the values of $P_m Q_n - Q_m P_n$ for the earlier values of n. We have, if P's of negative order are properly interpreted as zero,

$$Q_n = \tfrac{1}{2} P_n \log \frac{1+\mu}{1-\mu} - \left\{ \frac{2n-1}{1\,.\,n} P_{n-1} + \frac{2n-5}{3\,.\,n-1} P_{n-3} + \frac{2n-9}{5\,.\,n-2} P_{n-5} + \ldots\ldots \right\},$$

$$Q_0 = \tfrac{1}{2} \log \frac{1+\mu}{1-\mu},$$

$$\begin{aligned} P_m Q_0 - Q_m P_0 &= \frac{2m-1}{1\,.\,m} P_{m-1} + \frac{2m-5}{3\,.\,m-1} P_{m-3} + \ldots\ldots \\ &= \frac{2m-1}{m} \left\{ P_{m-1} + \frac{1}{3} \cdot \frac{2m\,.\,2m-5}{2m-2\,.\,2m-1} P_{m-3} + \ldots\ldots \right\} \\ &= \frac{2m-1}{m} \cdot y_0. \end{aligned}$$

Again,

$$P_m Q_1 - Q_m P_1 = -P_m + \mu \left\{ \frac{2m-1}{1\,.\,m} P_{m-1} + \frac{2m-5}{3\,.\,m-1} P_{m-3} + \ldots\ldots \right\},$$

and using the recurrence formula

$$\overline{2r+1}\,.\,\mu P_r = \overline{r+1}\,.\,P_{r+1} + r P_{r-1},$$

we readily find that P_m disappears, and the result

$$P_m Q_1 - Q_m P_1 = \frac{2m-1\,.\,2m-3}{3m\,.\,m-1} y_1$$

is obtained,—a series beginning with P_{m-2}. Further, by the recurrence formula,

$$\begin{aligned} P_m Q_2 - Q_m P_2 &= \tfrac{1}{2} P_m (3\mu Q_1 - Q_0) - \tfrac{1}{2} Q_m (3\mu P_1 - P_0) \\ &= \frac{3\mu}{2} (P_m Q_1 - Q_m P_1) - \tfrac{1}{2} (P_m Q_0 - Q_m P_0) \\ &= \frac{3\mu}{2} \left(\frac{2m-1\,.\,2m-3}{3m\,.\,m-1} \right) y_1 - \frac{1}{2} \cdot \frac{2m-1}{m} \cdot y_0. \end{aligned}$$

Reduction of this expression, by use of the recurrence formula in the first term, readily shows that the coefficient of P_{m-2} now vanishes, and that the final result is

$$P_m Q_2 - Q_m P_2 = \frac{2}{3\,.\,5} \cdot \frac{2m-1\,.\,2m-3\,.\,2m-5}{m\,.\,m-1\,.\,m-2} y_2.$$

The next formula obtained in the same manner is

$$P_m Q_3 - Q_m P_3 = \frac{2}{5.7} \frac{2m-1 \,.\, 2m-3 \,.\, 2m-5 \,.\, 2m-7}{m \,.\, m-1 \,.\, m-2 \,.\, m-3} \,.\, y_3,$$

the work becoming laborious at this point. But the nature of the final result is already clear, and a proof by induction can at once be given. If we suppose that, when $m>n$,

$$P_m Q_n - Q_m P_n = f(n) \,.\, \frac{2m-1 \,.\, 2m-3 \,.\, \ldots\, 2m-2n-1}{m \,.\, m-1 \,.\, m-2 \,.\, \ldots\, m-n} \, y_n,$$

where y_n is the series denoted by *Series C*, and $f(n)$ is a function only of n, and not m, we can show, by use of the fact that

$$(n+1)(P_m Q_{n+1} - Q_m P_{n+1})$$
$$= (2n+1)\mu(P_m Q_n - Q_m P_n) - n(P_m Q_{n-1} - Q_m P_{n-1})$$

that the formula is true universally, and that

$$f(n) = \frac{n}{2n+1} f(n-1).$$

This latter relation is also clearly satisfied by the initial values, for

$$f(0)=1, \quad f(1)=\frac{1}{3}, \quad f(2)=\frac{2}{3.5}, \quad f(3)=\frac{2}{5.7},$$

which are perhaps in themselves sufficient to suggest the relation. Finally, if $m>n+1$,

$$P_m Q_n - Q_m P_n = f(n) \frac{2m-1 \,.\, 2m-3 \,.\, \ldots\, 2m-2n-1}{m \,.\, m-1 \,.\, m-2 \,.\, \ldots\, m-n} y_n,$$

where

$$f(n) = \frac{n}{2n+1} f(n-1) = \frac{n(n-1)}{2n+1 \,.\, 2n-1} f(n-2) = \ldots.$$

$$= \frac{n \,.\, n-1 \,.\, n-2 \,.\, n-3 \,.\, \ldots\, 1 f(0)}{2n+1 \,.\, 2n-1 \,.\, 2n-3 \,.\, \ldots\, 3} = \frac{n\,!}{3 \,.\, 5 \,.\, \ldots\, 2n+1}$$

$$= \frac{2^n (n\,!)^2}{2n+1\,!},$$

$$P_m Q_n - Q_m P_n$$

$$= y_n \,.\, \frac{2^n (n\,!)^2\, m-n-1\,!}{2n+1\,!\; m\,!} \; \frac{2m\,!}{2m-2n-2\,!} \; \frac{m-n-1\,!}{2^{n+1}\, m\,!};$$

or finally, if $m > n+1$,

$$\mathrm{P}_m \mathrm{Q}_n - \mathrm{Q}_m \mathrm{P}_n$$

$$= \frac{1}{2}\left(\frac{n\,!}{m\,!}\right)^2 \cdot \frac{2m\,!\,(m-n-1\,!)^2}{2n+1\,!\;2m-2n-2\,!}\left\{\mathrm{P}_{m-n-1} + \right.$$

$$+ \frac{1}{2} \cdot \frac{2m\,.\,2n+2\,.\,2m-2n-1\,.\,2m-2n-5}{2m-1\,.\,2n+3\,.\,2m-2n-2\,.\,2m-2n-1}\mathrm{P}_{m-n-3} +$$

$$+ \frac{1\,.\,3}{2\,.\,4} \cdot \frac{2m\,.\,2m-2}{2m-1\,.\,2m-3} \cdot \frac{2n+2\,.\,2n+4}{2n+3\,.\,2n+5}$$

$$\left. \cdot \frac{2m-2n-1\,.\,2m-2n-3}{2m-2n-2\,.\,2m-2n-4} \cdot \frac{2m-2n-9}{2m-2n-1}\mathrm{P}_{m-n-5} + \ldots\right\}$$

If $m=n+1$, the expression is known to be constant. If $m=n$, it is zero. It is constant again if $m=n-1$, and if $n > m+1$ the factorials clearly only need re-writing. If expressed as Gamma functions, the same theorem is true throughout.

Series for $\mathrm{Q}_{2m}\mathrm{P}_n$.

We know that

$$\mathrm{Q}_{2m}(\mu) = -2\,\Sigma_0^\infty \frac{(4r+3)\,\mathrm{P}_{2r+1}}{2m-2r-1\,.\,2m+2r+2} \doteq \mathrm{Q}_{2m}(\mu)\,\mathrm{P}_0(\mu).$$

Thus, multiplying by μ, and using a recurrence formula,

$$-\tfrac{1}{2}\mathrm{Q}_{2m}\mathrm{P}_1 = \Sigma_0^\infty \frac{4r+3}{2m-2r-1\,.\,2m+2r+2}$$

$$\times \left\{\frac{2r+2\,.\,\mathrm{P}_{2r+2} + 2r+1\,.\,\mathrm{P}_{2r}}{4r+3}\right\}$$

$$= \frac{\mathrm{P}_0}{2m-1\,.\,2m+2} + \Sigma_0^\infty \left\{\frac{2r+1}{2m-2r-1\,.\,2m+2r+2}\right.$$

$$\left. + \frac{2r}{2m-2r+1\,.\,2m+2r}\right\}\mathrm{P}_{2r},$$

which, on reduction, becomes

$$-\tfrac{1}{2}\mathrm{Q}_{2m}\mathrm{P}_1$$

$$= \Sigma_0^\infty \frac{4r+1\,.\,2m-2r\;\;2m+2r+1}{2m-2r-1\,.\,2m+2r+2\,.\,2m-2r+1\,.\,2m+2r}\mathrm{P}_{2r},$$

the term P_0 falling naturally into the series.

Again,

$$-\tfrac{1}{2}Q_{2m}P_2$$

$$=-\tfrac{1}{4}Q_{2m}\{3\mu P_1-P_0\}$$

$$=\tfrac{3}{2}\Sigma_0\frac{4r+1\,.\,2m-2r\,.\,2m+2r+1}{2m-2r-1\,.\,2m+2r+2\,.\,2m-2r+1\,.\,2m+2r}\,.\left\{\frac{2r+1\,.\,P_{2r+1}+2r\,P_{2r-1}}{4r+1}\right\}$$

$$-\tfrac{1}{2}\Sigma_0^{\infty}\frac{4r+3\,.\,P_{2r+1}}{2m-2r-1\,.\,2m+2r+2}.$$

After a fair amount of reduction, this becomes

$$-\tfrac{1}{2}Q_{2m}P_2=\Sigma_0^{\infty}\frac{4r+3\,.\,2m-2r\,.\,2m-2r-2\,.\,2m+2r+1\,.\,2m+2r+3\,.\,P_{2r+1}}{2m-2r-3\,.\,2m-2r-1\,.\,2m-2r+1\,.\,2m+2r\,.\,2m+2r+2\,.\,2m+2r+4}.$$

and indications of a general formula are already apparent.

Continuing this procedure, we are able to show that

$$-\tfrac{1}{2}Q_{2m}P_3$$

$$=\Sigma_0^{\infty}\frac{4r+3\,(2m-2r+2\,.\,2m-2r\,.\,2m-2r-2)\,.\,(2m+2r-1\,.\,2m+2r+1\,.\,2m+2r+3)}{(2m-2r-3\,.\,2m-2r-1\,.\,2m-2r+1\,.\,2m-2r+3)\,.\,(2m+2r\,.\,2m+2r+2\,.\,2m+2r+4\,.\,2m+2r+6)}P_{2r}.$$

These forms may be shortened to

$$-\tfrac{1}{2}Q_{2m}P_0=\Sigma_0^{\infty}\frac{4r+3\,.\,P_{2r+1}}{2m\,.\,2m+1-2r+1\,.\,2r+2},$$

$$-\tfrac{1}{2}Q_{2m}P_1=\Sigma_0^{\infty}\frac{4r+1\,.\,P_{2r}}{2m\,.\,2m+1-2r+1\,.\,2r+2}\,.\frac{2m\,.\,2m+1-2r\,.\,2r+1}{2m\,.\,2m+1-2r-1\,.\,2r},$$

$$-\tfrac{1}{2}Q_{2m}P_2=\Sigma_0^{\infty}\frac{4r+3\,P_{2r+1}}{2m\,.\,2m+1-2r+1\,.\,2r+2}\,.\frac{2m\,.\,2m+1-2r\,.\,2r+1}{2m\,.\,2m+1-2r-1\,.\,2r}\,.\frac{2m\,.\,2m+1-2r+2\,.\,2r+3}{2m\,.\,2m+1-2r+3\,.\,2r+4}.$$

The next quotient, appearing first in $-\frac{1}{2}Q_{2m}P_3$, is

$$\frac{2m\,.\,2m+1-2r-2\,.\,2r-1}{2m\,.\,2m+1-2r-3\,.\,2r-2}.$$

It is suggested that the general formula is as follows:—

If

$$f(s)=2m\,.\,2m+1-s\,.\,s+1=2m-s\,.\,2m+s+1,$$

then

$$-\tfrac{1}{2}Q_{2m}P_{2n}=\Sigma_0^\infty\frac{4r+3\,.\,P_{2r+1}}{f(2r+1)}\;\frac{f(2r)}{f(2r-1)}\;\frac{f(2r+2)}{f(2r+3)}\cdot\frac{f(2r-2)}{f(2r-3)}$$

$$\cdot\frac{f(2r+4)}{f(2r+5)}\cdot\frac{f(2r-4)}{f(2r-5)}\cdot\frac{f(2r+6)}{f(2r+7)}\cdot\cdots$$

$$\cdot\frac{f(2r-2n+2)}{f(2r-2n+1)}\cdot\frac{f(2r+2n)}{f(2r+2n+1)},$$

and the reader will be able to prove by induction, following the above method, that this is correct. The analysis is in no way more complicated than that involved in deducing the preceding expressions.

The coefficient of P_{2r+1} in this expression is $(4r+3)S$, where

$$S=\frac{f(2r-2n+2)\;f(2r-2n+4)\;\ldots\;f(2r+2n)}{f(2r-2n+1)\;f(2r-2n+3)\;\ldots f(2r+2n+1)},$$

and since

$$f(s)=(2m-s)(2m+s+1)$$

this becomes

$$S=S_1S_2,$$

where

$$S_1=\frac{2m+2r-2n+3\,.\,2m+2r-2n+5\,.\,\ldots\,.\,2m+2r+2n+1}{2m+2r-2n+2\,.\,2m+2r-2n+4\,.\,\ldots\,.\,2m+2r+2n+2}$$

$$=\frac{1}{2}\cdot\frac{\Gamma(m+n+r+\frac{3}{2})}{\Gamma(m-n+r+\frac{3}{2})}\cdot\frac{\Gamma(m-n+r+1)}{\Gamma(m+n+r+2)}$$

and

$$S_2=\frac{2m-2r+2n-2\,.\,2m-2r+2n-4\,.\,\ldots\,.\,2m-2r-2n}{2m-2r+2n-1\,.\,2m-2r+2n-3\,.\,\ldots\,.\,2m-2r-2n-1}$$

$$=\frac{1}{2}\cdot\frac{\Gamma(m+n-r)}{\Gamma(m-n-r)}\cdot\frac{\Gamma(m-n-r-\frac{1}{2})}{\Gamma(m+n-r+\frac{1}{2})},$$

and finally, we derive the remarkable formula

$$Q_{2m}(\mu)\,P_{2n}(\mu) = -\frac{1}{2}\sum_{r=0}^{\infty}(4r+3)\frac{\Gamma(m+n-r)}{\Gamma(m-n-r)}\cdot\frac{\Gamma(m-n+r+1)}{\Gamma(m+n+r+2)}$$

$$\cdot\frac{\Gamma(m-n-r-\frac{1}{2})}{\Gamma(m+n-r+\frac{1}{2})}\cdot\frac{\Gamma(m+n+r+\frac{3}{2})}{\Gamma(m-n+r+\frac{3}{2})}P_{2r+1}(\mu),$$

where m and n are integers.

There is nothing in our argument which causes it to fail when n is pushed to a value exceeding m, and the formula is therefore general.

The only two Gamma functions which can ever become infinite are $\Gamma(m-n-r)$ in the denominator, and $\Gamma(m+n-r)$ in the numerator. The former must occur first, and when it does occur, in the first term (when $n>m$), the earlier part of the series vanishes, and we obtain a series starting with the harmonic $P_{2m+2n+1}$.

If $m>n$, this series so obtained is accompanied by another of a terminating type,—a gap lying between the two,—and this other is of course found to be a multiple of the series representing

$$P_{2m}Q_{2n}-Q_{2m}P_{2n}$$

and already discussed.

It is more convenient, however, not to separate the two cases, but to include both in the general formula expressed in terms of Gamma functions.

The single series obtained when $n>m$ is found to be a multiple of our *Series A*, found from the differential equation. This series is therefore recognized in terms of the solution it represents.

The preceding discussion has proceeded on the supposition that the order of both P and Q is even. When this is not the case, the analysis is very similar, and we may leave it to the reader to prove the following theorems, where m and n are integers in all cases :—

$$Q_{2m+1}(\mu)\,P_{2n+1}(\mu)$$

$$= -\frac{1}{2}\sum_{r=0}^{\infty}(4r+3)\frac{\Gamma(m+n-r+1)}{\Gamma(m-n-r)}\cdot\frac{\Gamma(m-n+r+1)}{\Gamma(m+n+r+3)}$$

$$\cdot\frac{\Gamma(m-n-r-\frac{1}{2})}{\Gamma(m+n-r+\frac{3}{2})}\cdot\frac{\Gamma(m+n+r+\frac{5}{2})}{\Gamma(m-n+r+\frac{3}{2})}\cdot P_{2r+1}(\mu),$$

$$Q_{2m}(\mu)\,P_{2n+1}(\mu)$$

$$= -\frac{1}{2}\sum_{r=0}^{\infty}(4r+1)\frac{\Gamma(m+n-r+1)}{\Gamma(m-n-r)}\cdot\frac{\Gamma(m-n+r)}{\Gamma(m+n+r+1)}$$

$$\cdot\frac{\Gamma(m-n-r-\frac{1}{2})}{\Gamma(m+n-r+\frac{3}{2})}\cdot\frac{\Gamma(m+n+r+\frac{3}{2})}{\Gamma(m-n+r+\frac{1}{2})}\,P_{2r}(\mu),$$

$$Q_{2m+1}(\mu)\,P_{2n}(\mu)$$

$$= -\frac{1}{2}\sum_{r=0}^{\infty}(4r+1)\frac{\Gamma(m+n-r+1)}{\Gamma(m-n-r+1)}\cdot\frac{\Gamma(m-n+r+1)}{\Gamma(m+n+r+2)}$$

$$\cdot\frac{\Gamma(m-n-r+\frac{1}{2})}{\Gamma(m+n-r+\frac{3}{2})}\cdot\frac{\Gamma(m+n+r+\frac{3}{2})}{\Gamma(m-n+r+\frac{3}{2})}\cdot P_{2r}(\mu).$$

The Value of an Integral.

We can now determine the value of the important integral

$$I = \int_{-1}^{1} P_\alpha\,P_\beta\,Q_\gamma\,d\mu,$$

where α, β, γ are integers. The integrand is odd or even in μ according as $\alpha+\beta+\gamma$ is even or odd. Thus the integral is zero if $\alpha+\beta+\gamma$ is even.

When $\alpha+\beta+\gamma$ is odd, various cases arise above. Thus

$$\int_{-1}^{1} Q_{2m}\,P_{2n}\,P_{2r+1}\,d\mu = -\frac{\Gamma(m+n-r)}{\Gamma(m-n-r)}\,\frac{\Gamma(m-n+r+1)}{\Gamma(m+n+r+2)}$$

$$\cdot\frac{\Gamma(m-n-r-\frac{1}{2})}{\Gamma(m+n-r+\frac{1}{2})}\cdot\frac{\Gamma(m+n+r+\frac{3}{2})}{\Gamma(m-n+r+\frac{3}{2})},$$

since

$$\int_{-1}^{1}(P_{2r+1})^2\,d\mu = \frac{2}{4r+3}, \qquad \int_{-1}^{1} P_{2r+1}\,P_{2s+1}\,d\mu = 0.$$

Again,

$$\int_{-1}^{1} Q_{2m}\,P_{2n+1}\,P_{2r}\,d\mu = -\frac{\Gamma(m+n-r+1)}{\Gamma(m-n-r)}\cdot\frac{\Gamma(m-n+r)}{\Gamma(m+n+r+1)}$$

$$\cdot\frac{\Gamma(m-n-r-\frac{1}{2})}{\Gamma(m+n-r+\frac{3}{2})}\cdot\frac{\Gamma(m+n+r+\frac{3}{2})}{\Gamma(m-n+r+\frac{1}{2})}.$$

There are four such cases in all. We find that they can all be expressed by the single formula

$$\int_{-1}^{1} P_\alpha P_\beta Q_\gamma \, d\mu = -\frac{\Gamma\left(\frac{\gamma-\alpha-\beta}{2}\right)}{\Gamma\left(\frac{\gamma-\alpha-\beta+1}{2}\right)} \cdot \frac{\Gamma\left(\frac{\gamma+\alpha+\beta+2}{2}\right)}{\Gamma\left(\frac{\gamma+\alpha+\beta+3}{2}\right)}$$

$$\cdot \frac{\Gamma\left(\frac{\gamma+\alpha-\beta+1}{2}\right)}{\Gamma\left(\frac{\gamma+\alpha-\beta+2}{2}\right)} \cdot \frac{\Gamma\left(\frac{\gamma+\beta-\alpha+1}{2}\right)}{\Gamma\left(\frac{\gamma+\beta-\alpha+2}{2}\right)},$$

which is valid for all integer values of α, β, γ whose sum is odd. This result is symmetrical in α and β, as of course it should be.

Since $\gamma+\alpha+\beta$ is odd, the arguments of the Γ functions in the numerator, capable of becoming negative, are

$$\tfrac{1}{2}\{\gamma-\alpha-\beta, \quad \gamma+\alpha-\beta+1, \quad \gamma+\beta-\alpha+1\}$$

or

$$\tfrac{1}{2}(\gamma+\alpha+\beta)-(\alpha+\beta), \quad \tfrac{1}{2}(\gamma+\alpha+\beta+1)-\beta,$$
$$\tfrac{1}{2}(\gamma+\alpha+\beta+1)-\alpha.$$

The first cannot be an integer, $\gamma+\alpha+\beta$ being odd. The others can, but if they are integers of negative sign, the function

$$\Gamma\left(\frac{\gamma-\alpha-\beta+1}{2}\right)$$

in the denominator is of the same type, so that the limiting value is always finite.

There are interesting cases in which the integral is zero when $\alpha+\beta+\gamma$ is odd. This occurs, for example, if

$$\frac{\gamma-\alpha-\beta+1}{2}$$

is a negative integer (or zero), or if $\alpha+\beta-\gamma$ *is an odd positive integer.* This in fact includes all cases, when $\alpha+\beta+\gamma$ is odd. Thus the integral

$$\int_{-1}^{1} P_\alpha P_\beta Q_\gamma \, d\mu = 0$$

when (1) $\alpha+\beta+\gamma$ is even and (2) $\alpha+\beta+\gamma$ is odd, and $\alpha+\beta-\gamma$ is positive. It is always zero if $\alpha+\beta$ is greater than γ.

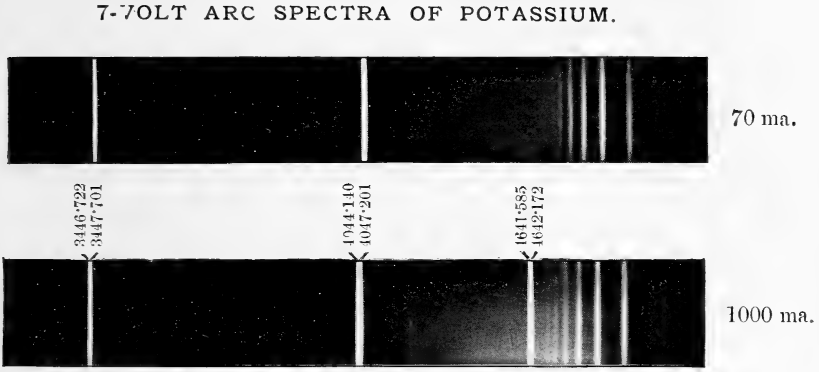
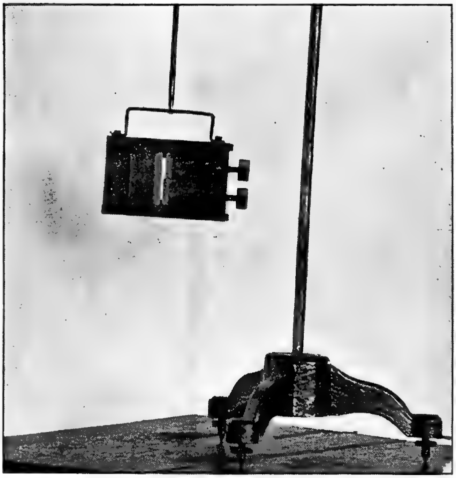


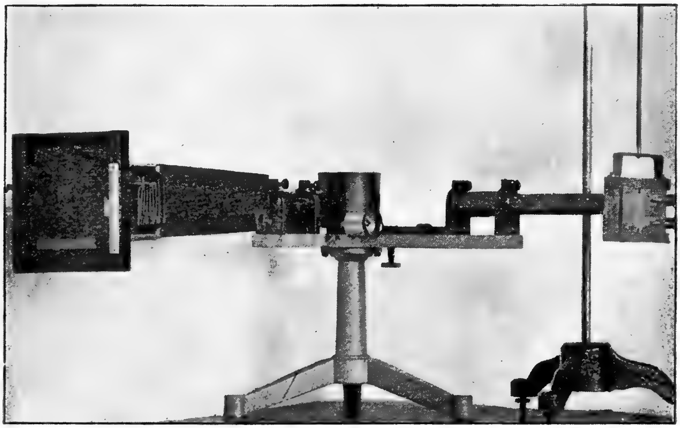
FIG. 2.—The arc spectrum of potassium obtained with a hot-cathode tube similar to that shown by fig. 1. The pair 1s–3d appears very prominently at 1000 milliamperes and 7 volts. This is an exception to the principle of selection, since the change in azimuthal quantum number is two units, which cannot be attributed to a Stark effect.

FIG. 1.



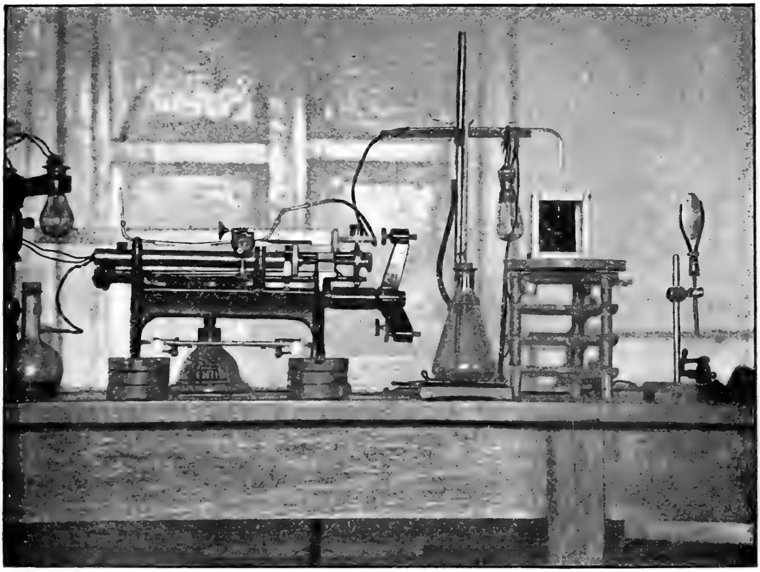
Spectrophotometer.

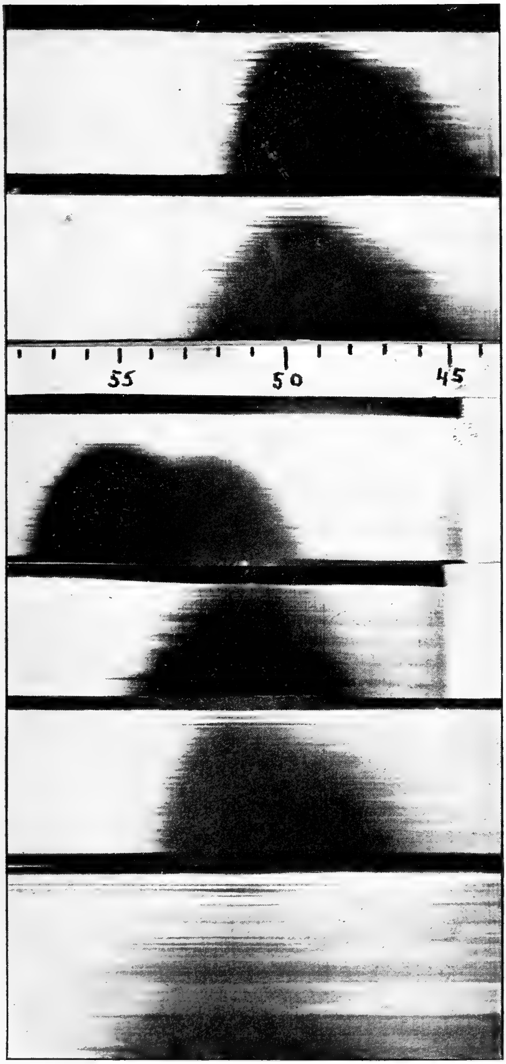
FIG. 2.



Spectrophotometer in position.

FIG. 1.





(Uranine)
Fluorescein.

Photo-
Fluorescein.

Rhodamine.

Photo-
Rhodamine.

Eosine.

Photo-
Eosine.

THE

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JOURNAL OF SCIENCE.

[SIXTH SERIES.]

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XCI. *Notes on the Kinetic Theory of Gases. Sutherland's constant S and van der Waals' a and their relations to the intermolecular field.* *By* R. H. Fowler, *Fellow and Lecturer of Trinity College, Cambridge* *.

§ (1). *Introduction and Summary.*—This paper consists of two somewhat loosely connected parts. In the first part, § 2, I point out the conditions under which a strict comparison may be made between the intermolecular fields deduced from Sutherland's constant S and from van der Waals' a. On comparing the numerical results I have then to point out a serious outstanding discrepancy between the values deduced in these two ways; I make a suggestion as to the probable source of this discrepancy, but have not yet resolved it in detail.

In the second part, §§ 3–11, I give two simple proofs of the exact formula for van der Waals' a as a function of the intermolecular field of force which I believe to be illuminating and new, or at least insufficiently known. The calculations are reduced to explicit formulæ for two particular molecular models:—

(1) Elastic spheres attracting according to an inverse sth power law.

(2) Elastic spheres surrounded by a limited spherical shell in which there is a *constant* attraction, with no forces at all outside.

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* Communicated by C. G. Darwin, M.A.

§ (2). *Sutherland's S and van der Waals' a.*—It is well known that both the constant S introduced by Sutherland* into the formula for the viscosity of a gas, and the constant *a* of van der Waals' or Dieterici's equations of state† express the effects of intermolecular attractions. On the assumption of "spherically symmetrical" molecules—*i. e.*, that the molecules are spheres and that the attractive force $\phi(r)$ between two molecules depends only on the distance r between their centres and acts along the line joining them—Chapman‡ has shown how to obtain an exact expression for S in terms of $\phi(r)$ and known constants. The most complete determination of *a* in terms of $\phi(r)$ with which I am acquainted has been made by Keesom§, but no attempt appears to have been made to compare together both theoretical and experimental values of *a* and S. This is the more to be regretted as the quantities *a* and S may be taken to refer to gases in identical physical states. A strict comparison of theory with the experimental values of *a* and S is then legitimate, and should lead to results of interest as to the nature of the law of intermolecular attraction under these conditions.

When we come to compare *a* with experiment, we must remember that our theoretical calculations only apply to gases at reasonably large dilutions, that is to cases in which the departures from the perfect gas laws are moderately small. In order to make a reliable comparison between theory and experiment we must therefore be certain that the observations and calculations do actually apply strictly to one and the same state of the gas. The calculations used really always present the equation of state of a gas in the form

$$pv = \mathrm{N}k\mathrm{T} + \frac{1}{v}f(\mathrm{T}) + \mathrm{O}\left(\frac{1}{v^2}\right)\|, \quad . \quad . \quad . \quad . \quad (1)$$

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* Sutherland, Phil. Mag. ser. 5, vol. xxxvi. p. 507 (1893) and succeeding vols.

† Jeans, 'The Dynamical Theory of Gases,' ed. 3, chap. 6 (1921).

‡ Chapman, Phil. Trans. A, vol. 211. p. 460 (1912). The actual formula given by Chapman is affected by an algebraical slip. The correct expressions have been given by C. G. F. James, Proc. Camb. Phil. Soc. vol. xx. p. 447 (1921), and previously in part by D. Enskog, Inaugural-Dissertation, Uppsala 1917, p. 95.

§ Keesom, Proc. Sect. of Sciences, Amsterdam, vol. xv. (1) pp. 240, 256, 417, 643 (1912).

‖ $\mathrm{O}\left(\frac{1}{v^2}\right)$ is a convenient and comprehensive notation for "terms of order $1/v^2$, which may therefore be neglected for values of v which are sufficiently large." This is a satisfactory paraphrase of the strict mathematical definition of O, to which of course I adhere throughout.

where p is the pressure, v the volume, k the gas-constant for one molecule, N the number of molecules, and $f(T)$ is a function of the absolute temperature T which can be calculated exactly. Now it is precisely in this form that Kamerlingh Onnes has prepared his extensive data on the equations of state of the simpler gases. Actually * he assumes the form

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8}, \quad . \quad . \quad . \quad (2)$$

and determines A, ..., F as functions of T to fit the observations. The coefficients A, ..., F he calls the first, second, etc., *virial coefficients.* It is clear that when the observed second virial coefficient B is obtained in this way it is strictly comparable to the calculated $f(T)$ of equation (1). Moreover, it appears to me that nothing much less than the exhaustive numerical analysis of Kamerlingh Onnes allows a legitimate comparison between theory and experiment to be made.

Such comparisons have already been made in certain cases and on certain assumptions by Keesom (*loc. cit.*), but without consideration of the corresponding viscosity data. I hope to take up the question in detail in a future paper. For the present I must content myself with the following observations. Keesom finds that the observed and calculated second virial coefficients for Argon, between the absolute temperatures 123° and 293° on the centigrade scale, can be reconciled on the assumption that the argon atom behaves like a sphere of diameter, $\sigma = 3{\cdot}29 \times 10^{-8}$ cm., surrounded by a field of force $\phi(r) = \alpha r^{-5}$, of such intensity that the work $\Pi(\sigma)$ done in separating two molecules from contact ($r = \sigma$) to infinity is $1{\cdot}63 \times 10^{-14}$ erg †. The exponent 5 is a little doubtful, but is probably better than the exponents 4 or 6 and presumably better than any other integral exponent.

These values of σ and $\phi(r)$ correspond to definite values of b (van der Waals') and S, Sutherland's constant. The values of b and σ are related by the well-known formula

$$b = \tfrac{2}{3}\pi N \sigma^3, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

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* Kamerlingh Onnes, Proc. Sect. of Sciences, Amsterdam, vol. iv. p. 125 (1902), or Communications Phys. Lab. of Leiden, No. 71.

† Keesom (*loc. cit.* p. 646) gives $1{\cdot}46 \times 10^{-14}$, but this is based on the incorrect value $6{\cdot}85 \times 10^{23}$ for Loschmidt's number. I have reworked the calculation with the more recent figure $6{\cdot}06 \times 10^{23}$.

and S is given by Chapman's corrected formula *

$$S = 0{\cdot}1956\,\Pi(\sigma)/k. \quad \text{(Inverse 5th-power attractions.)} \quad (4)$$

The numerical values deduced from Keesom's figures are $b=0{\cdot}00201$ for 1 c.c. at normal pressure and temperature, and $S=23{\cdot}6$. But the viscosity data for ordinary temperatures should be fairly comparable with the preceding "compressibility" data, and should lead to the same values of b, σ, $\Pi(\sigma)$, and S. When analysed, however, by Chapman's formulæ, they lead unmistakably to the values $b=0{\cdot}00133$, $S=162$. We may exhibit this significant discrepancy thus:—

Argon.

	$\Pi(\sigma)\times10^{14}$.	S.	$b\times10^{3}$.	$\sigma\times10^{8}$.
Compressibility data...	1·63	23·6	2·01	3·29
Viscosity data	11·2	162	1·33	2·84

The disagreement, particularly in the values of S and $\Pi(\sigma)$, is striking; so far as I know at present similar discrepancies occur for other gases besides argon, but the available data are not generally so suitable for a direct comparison. This disagreement is all the more interesting in view of the close agreement between the two values of σ (or b) given by Chapman † himself. But the values of b from the compressibility data there given appear to be obtained from critical data, and must in my opinion give way to values calculated from Kamerlingh Onnes' second virial coefficient.

The discrepancy which thus remains seems to arise from the fact that whereas the theoretical formula for the second virial coefficient B is exact, the formula used for the viscosity is only correct so far as the first power of S/T. The agreement of this approximate viscosity theory with experiment is usually regarded as good, at least at ordinary temperatures, so that an exact formula including further powers of S/T is not likely to improve this fit. It may well, however, bring the facts of compressibility and viscosity into reasonable agreement—in particular at fairly high temperatures, and so enable a reliable picture to be formed of the range and intensity (under these conditions) of the intermolecular forces.

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* Chapman gives $S=\Pi(\sigma)/3k$ in our notation for all power laws. The correction affects only the numerical coefficient which becomes a function of s the power law exponent (James, *loc. cit.*).

† Phil. Trans. A, vol. 216. Table VIII. p. 347 (1916).

The existing discrepancies in S and σ are qualitatively such as should be properly accountable for by such an extension of the theory; to this point I hope to return in a later paper.

Elementary calculations of van der Waals' a.

§ (3). My immediate object in the rest of this paper is to present two simple proofs of the exact formula for B, and so for van der Waals' a. Keesom has calculated B in terms of the intermolecular field by a somewhat elaborate method based on Boltzmann's expression for the entropy, a method which can be used when the molecules are not spherically symmetrical. But Keesom's own work shows that molecules with spherical symmetry give the best representation of experimental facts for the simplest (monatomic) gases. Such molecular models are therefore of the first importance, and for such it is possible to calculate B directly by very simple arguments—(1) By a direct calculation of the boundary field, measured by W, the work to be done in bringing a molecule from the interior to the boundary of the gas; or, (2) By a calculation of the Virial of Clausius.

Method (1) has moreover this advantage over all other methods, that it enables adequate account to be taken of surface effects, which is not possible, or at least far less simple, by the entropy and virial methods. In calculating B all the terms in pv of order $1/v^2$ are of course to be omitted.

§ (4). *The meaning of a.*—The so-called constant a of van der Waals' or Dieterici's equation of state can be specified in various ways. The most satisfactory physical meaning can be attached to it, by first recognizing [*] that intermolecular attractions must result in the production of a permanent field of force near any boundary of a gas, and then connecting a to the work that must be done against this boundary field in bringing one molecule from the interior to the actual boundary of the gas. At sufficiently great dilutions this work W must obviously be proportional to the molecular density ν, and it is easily proved that [†]

$$a = N^2 W/\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where N is the total number of molecules in the body of gas considered. Thus a will be independent of the *volume*.

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[*] Jeans, *loc. cit.* p. 159.

[†] Jeans, *loc. cit.*

It appears, however, to be generally assumed * that under the same conditions W, and therefore a, is independent also of the *temperature*, and that a is therefore, theoretically at least, a true constant. When one looks into this assumption more closely it is easy to convince oneself that it has no justification whatever, however great the dilution. The ordinary kinetic theory of gases really demands an a which is a function of the temperature whose variations for most gases are appreciable at ordinary and even at fairly high temperatures. It is the more unfortunate that this theoretical result is so often overlooked, since the independence of a of the temperature is not borne out by experiment. In point of fact, both theory and experiment demand variations of a with the temperature which are, qualitatively at any rate, in full agreement with one another.

As we shall see directly in calculating a, the error arises from regarding the gas molecules in the interior of the gas as uniformly distributed through its volume. But if there are attractive forces sufficient to create a boundary field, these attractive forces must also make it correspondingly more probable that any pair of molecules will be close together than far apart. This alters the calculated value of W by an amount which may be called *the clustering correction.* It appears on calculation that this clustering correction depends on the temperature, and at ordinary temperatures is in fact of the same order as the whole boundary field itself.

§ (5). *The dependence of a on the nature of the intermolecular forces.*—We have stated above that a is independent of the volume in the circumstances we contemplate here. It seems necessary even now to insist that this independence holds good whatever the nature of the intermolecular forces, and is in no way dependent on obedience to any special law of variation with distance such as for example the inverse 4th power law. It is still frequently stated † that if van der Waals' a is to be independent of the volume the law of attraction must be the inverse 4th power. This is quite untrue. As we shall see, the law of variation with the distance affects and only affects the form of a as a function of *the temperature.*

In the case of spherically symmetrical attractions following inverse sth power laws generally we can go further, for we find that the integrals that occur do not converge unless $s>4$. The physical meaning of this failure is easily seen to

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* Jeans, *loc. cit.*

† *E. g.*, Lewis, 'A System of Physical Chemistry,' vol. i. p. 8 (1918), and many recent papers in the Phil. Mag.

be that if $s \leq 4$ the attractions of distant molecules in the gas will then be of equal or greater importance than those of the neighbouring molecules. In such a case the recorded pressure at any point would be affected or even dominated by the distant attractions and would depend on the general shape of the whole body of gas. This is of course directly contrary to experience, and no such attractions of sensible magnitude[*] can be admitted.

Finally, it is interesting to observe that we can obtain the case $s=4$ as a limiting case in which the intensity of the intermolecular attraction between any pair of molecules tends to zero as $s \rightarrow 4$ from above. In this limiting case and this only, we do in fact obtain a value of a which is a true constant *independent of the temperature.* This, however, can only be achieved at the price of a zero value for $\Pi(\sigma)$, and therefore for Sutherland's constant; this is inadmissible in the case of any actual gas.

§(6). *The work done in bringing a molecule from the interior to the boundary of a gas.*—The molecular model that we consider is that of a hard elastic sphere of diameter σ, surrounded by a field of attractive force. Two molecules whose centres are distant r apart act on each other with an attraction $\phi(r)$ along their line of centres. It is this molecular model which is so successful in explaining the "transport phenomena" in gases and their variation with temperature at ordinary temperatures—in particular the coefficient of viscosity. When such fields of force are postulated, the distribution of molecules in the gas is not on the average uniform with reference to any selected molecule. If ν is the general molecular density in the gas, the molecular density at a distance r from the selected molecule is, not ν, but[†]

$$\nu e^{2j\int_r^\infty \phi(x)dx}, \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

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[*] Gravitational attractions are in this category, and are of course insensibly small. Electrostatic attractions are in the same category, but are so large that they entirely dominate the distribution of charged molecules or ions.

[†] See, *e. g.*, Boltzmann, *Vorlesungen über Gastheorie,* vol. ii. p. 150 or Jeans, *loc. cit.* p. 132. Jeans' suggested correction of this formula is here insensible. Owing to the standardization of the use of h for Planck's constant, I believe that the time has come for the use of some letter other than h for the constant in Maxwell's Law for the distribution of velocities, and I propose to use j for this purpose. I believe, further, that it is desirable to use a notation distinguishing systematically between "the gas-constant for one gramme-molecule" and "the gas-constant for one molecule" (the constant k in $2j=1/k\mathrm{T}$) and to conform to the continental notation of R and k respectively.

where $2j=1/kT$. Consider an infinite plane slab of thickness df, which is small compared with σ, and let us calculate the average attraction dF of all the molecules in this slab on a molecule distant z from the slab *. The calculation is a generalization of the classical calculation of Laplace's theory of surface tension †, generalized in such a way as to recognize the real molecular structure of the fluid.

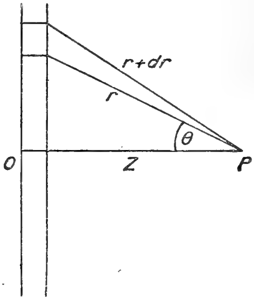
Suppose first that the selected molecule is at P and that $z \geqslant \sigma$. Then the average number of molecules in the slab, per unit area of the slab at a distance r from P, is

$$\nu df e^{2j\Pi(r)},$$

where we have written, for convenience,

$$\Pi(r)=\int_r^\infty \phi(x)\,dx. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Fig. 1.



The number in the annulus at distances between r and $r+dr$ from P is

$$2\pi r \sin\theta \,.\, \frac{dr}{\sin\theta} \,.\, \nu df e^{2j\Pi(r)},$$

and their resultant attraction along PO is

$$2\pi\nu z\, df\, \phi(r) e^{2j\Pi(r)} dr. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

To obtain the attraction of the whole slab, we must integrate the expression for values of r from z to infinity.

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* For shortness a molecule is said to be in the slab or distant z from the slab, when its *centre* is in or distant z from the slab.

† See, *e. g.* Rayleigh, Scientific Papers, vol. iii. pp. 397, 513 (1890, 1892); 'The Theory of Surface Forces.'

Since $\phi(r)=-\Pi'(r)$, it can be integrated in finite terms, giving

$$dF=\frac{2\pi\nu z\,df}{2j}(e^{2j\Pi(z)}-1), \quad (z>\sigma) \quad . \quad . \quad . \quad (8)$$

When $z\leq\sigma$ the conditions change, for now the body of the selected molecule prevents any attracting molecule from being present in the slab for values of r less than σ. The total attraction of the slab is therefore obtained by replacing z, the lower limit of integration, by σ, and we have

$$dF=\frac{2\pi\nu z\,df}{2j}(e^{2j\Pi(\sigma)}-1), \quad (z\leq\sigma). \quad . \quad . \quad . \quad (9)$$

Formulæ (8) and (9) can be combined into the single formula

$$dF=\frac{2\pi\nu z\,df}{2j}(e^{2j\Pi(z)}-1), \quad . \quad . \quad . \quad . \quad (10)$$

valid for all values of z, if we make the convention that

$$\Pi(z)=\Pi(\sigma), \quad (0\leq z\leq\sigma). \quad . \quad . \quad . \quad (11)$$

As $\Pi(z)$ is meaningless so far as equation (6) is concerned for such values of z, there is no objection to this convention.

It follows at once that the work done by the attractions of the slab when the molecule is brought from infinity to z is

$$\frac{2\pi\nu\,df}{2j}\int_r^\infty u(e^{2j\Pi(u)}-1)\,du\,;$$

it is convenient to have a notation for this expression, and we shall call it

$$2\pi\nu\,df\varpi(z).$$

It is obvious from the symmetry that we must have

$$\varpi(z)=\varpi(-z)\,;$$

just as much work is done by the attractions when the molecule is brought from infinity to $+z$ as when it is brought right through the slab to $-z$.

Consider a boundary surface of a body of gas, which may be supposed to extend to infinity in the direction of the positive axis of z. When a boundary field exists, the general molecular density in any slab must be a function $\nu(f)$ of f the distance from the boundary. The boundary of any actual vessel may in general be regarded as plane since the curvature will be negligible compared with the scale of molecular sizes and distances with which we are concerned.

The total work $\chi(z)$ done by the attractions of all slabs when a molecule is brought from positive infinity in the gas to the distance z from the boundary of the gas, which may be supposed to be the plane $z=0$ *, is therefore given by the equation

$$\chi(z)=2\pi\int_0^\infty \varpi(z-f)\nu(f)df. \quad . \quad . \quad . \quad (12)$$

§ (7). *The effect of variation of* ν *with* f.—So far our arguments are quite general, provided only that the molecular density in the neighbourhood of a selected molecule is adequately given by (5 a). This expression must fail at sufficiently great concentrations, for the gas may for example be so dense that no excess concentration in the neighbourhood of any molecule is physically possible. It is easily seen that the necessary correction can be introduced in the usual way by taking account of the presence of one molecule in affecting the chances for the presence of a second etc., and that such corrections must result in terms of order $1/\nu$, $1/\nu^2$, ..., compared to the leading terms in W. They are therefore irrelevant in the calculation of B from equation (12).

To proceed further with (12) we require the molecular density $\nu(f)$ as a function of f the distance from the boundary. It turns out that the effect of this variation is also of order $1/\nu$ and irrelevant for our present purposes. This may be seen as follows. It is well known † that $\nu(f)$ depends on f (a) because of the existence of the field of force of potential $\chi(\infty)-\chi(f)$, and (b) because the molecules are of finite size. Jeans gives an expression for $\nu(0)$ which takes account of the first-order correction for the size of the molecules and of the complete effect of the field of force. It is easy to extend the method so as to calculate not only $\nu(0)$ but also $\nu(f)$ to the same order of accuracy.

Ignoring details we may write this expression for $\nu(f)$ in the form

$$\nu(f)=\nu e^{-2j(\chi(\infty)-\chi(f))}\{1+\nu e^{-2j(\chi(\infty)-\chi(f))}\phi(f,j,\sigma)\}, \quad (13)$$

where the function ϕ depends only on those variables which are explicitly mentioned. If we combine together (12) and

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* The strict meaning of this statement is that when the centre of the molecule lies in the plane $z=0$, the molecule is in contact with the rigid boundary of the vessel (supposed plane).

† Jeans, *loc. cit.* pp. 154–164. Jeans denotes our $\nu(0)$ by ν_b.

(13) we obtain the following integral equation for $\chi(z)$, namely,

$$\frac{\chi(z)}{2\pi\nu}=\int_0^\infty \varpi(z-f)e^{-2j(\chi(\infty)-\chi(f))}\{1+\nu e^{-2j(\chi(\infty)-\chi(f))}\phi(f,j,\sigma)\}\,df. \quad . \quad . \quad . \quad (14)$$

Further corrections for the size of molecules beyond the first-order correction result in a series of similar terms ν^2, ν^3, ..., on the right-hand side.

This is an integral equation of an unusual type. A formal proof that it has a unique solution would not (apparently) be particularly difficult. The relevant point at the moment is that the form of (14) shows that the first approximation to the solution (ν small, v large) must be of the form

$$\frac{\chi(z)}{2\pi\nu}=\int_0^\infty \varpi(z-f)\,df+O\left(\frac{1}{v}\right), \quad . \quad . \quad . \quad (15)$$

and therefore that in calculating B we should ignore all boundary variations of $\nu(f)$, and replace $\nu(f)$ by ν in equation (12).

§ (8). Continuing the calculations of § 6 in view of the discussion of § 7, we find that, to the required order,

$$\begin{aligned}\chi(z)&=2\pi\nu\int_0^\infty \varpi(z-f)\,df,\\ &=2\pi\nu\int_0^z \varpi(f)\,df+2\pi\nu\int_0^\infty \varpi(f)\,df. \quad . \quad . \quad . \quad (16)\end{aligned}$$

Using the definition of $\varpi(z)$ we obtain after reduction (integration by parts)

$$\begin{aligned}\chi(z)=\frac{2\pi\nu}{2j}\Big\{&\int_0^\infty (z+x)(e^{2j\Pi(x)}-1)\,x\,dx\\ &-\int_0^z (z-x)(e^{2j\Pi(x)}-1)\,x\,dx\Big\}. \quad . \quad . \quad . \quad (17)\end{aligned}$$

From equation (17) it follows at once that

$$\chi(0)=\tfrac{1}{2}\chi(\infty)=\frac{2\pi\nu}{2j}\int_0^\infty x^2(e^{2j\Pi(x)}-1)\,dx. \quad . \quad (18)$$

One would expect *a priori* $\chi(\infty)$ to vanish. The fact that it does not do so is due to the artificial nature of the assumed infinity conditions. And in fact it does not matter, for $\chi(\infty)$ means the work done *by* the attractions when the molecule is brought from positive infinity (in the gas) to a point in the gas which is still (practically) at an infinite distance from the boundary $z=0$. In the same way $\chi(0)$ means the work done *by* the attractions when the molecule is brought to the boundary itself. Whatever the infinity conditions, the work W done *against* the attractions when a molecule is brought to the boundary must be given by

$$W=\chi(\infty)-\chi(0)=\chi(0),$$

and we have from (5),

$$a=\frac{N^2\chi(0)}{\nu}=\frac{2\pi N^2}{2j}\int_0^\infty x^2(e^{2j\Pi(x)}-1)dx. \quad . \quad (19)$$

From (19) we can calculate a without much trouble for any reasonable law of force.

§ (9). *The correct value of van der Waals' b.*—The correct value of the second virial coefficient is of course given by van der Waals' or Dieterici's equations of state in the form

$$NkTb-a,$$

provided correct values of a and b are used. The correct value of a is given by (19). It is usually assumed that $b=\frac{2}{3}\pi N\sigma^3$, but when intermolecular attractions exist, this is no longer correct, but we must have

$$b=\frac{2}{3}\pi N\sigma^3 e^{2j\Pi(\sigma)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

a result which is often overlooked. Consider, for example, the proof of the usual formula for b given by Jeans [*]. He first obtains expressions for the excluded regions of the usual generalized space, and allows for them on the usual assumption that the *a priori* probability for the presence of a molecule in any element of generalized space is the same. To allow, for example, for the excluded region,

$$\Sigma(x_a-x_b)^2<\sigma^2$$

on this assumption of the equal probability of all positions of the b-molecule, we must exclude a fraction $\frac{4}{3}\pi\sigma^3/\Omega$ of the total generalized space Ω^N. But when there are central forces acting between the molecules we are no longer at liberty to assume that this *a priori* equal probability for elements of *generalized* space implies equal probabilities for equal volume elements in *ordinary* space. The correcting term must be multiplied by the probability of another molecule being at a distance σ from the selected molecule—

[*] *Loc. cit.* p. 157.

that is to say by $e^{2j\Pi(\sigma)}$. Making this correction the value of b given by (20) follows at once by the usual arguments. Equations (19) and (20) used in the ordinary formula $NkTb-a$ must give the exact form for the second virial coefficient.

We may note here the differences between the usual values of a and b and the values given by (19) and (20). The usual values are really obtained on the assumption that $2j\Pi(\sigma)$ is small so that $e^{2j\Pi(\sigma)}$ is very nearly unity, and the effect of this factor on a and b negligible. The value of a so obtained is of course

$$a=2\pi N^2\int_0^\infty x^2\Pi(x)\,dx.$$

It is most important to recognize *that increasing the dilution has no effect whatever on the accuracy or inaccuracy of this approximation*, for it does not affect $2j\Pi(\sigma)$. The approximation can only be justified *if the temperature is sufficiently high*. But by equation (4) $2j\Pi(\sigma)$ is of the order $5S/T$. For an ordinary monatomic or diatomic gas, whose viscosity is analysed by Sutherland's formula, $S>100$. [The only exceptions are He, H_2, and Ne.] Analysed by a more exact formula, taking account of all powers of $1/T$, a considerably smaller value of S (perhaps 5–10 times smaller) might fit the observations, and agree with the compressibility data (see § 2). But even so, $2j\Pi(\sigma)$ is about unity at a temperature of 100° absolute, and can hardly be considered small at temperatures less than 1000° absolute. It is not till we reach these temperatures that the clustering effect can be ignored, and the gas regarded as genuinely of uniform density throughout.

§ (10). *The direct calculation of the Virial of Clausius.*—It is possible to calculate independently by this method the exact value of the coefficient of $1/v$ in the expression for pv, and so confirm the results of the last section. The virial method is, however, unsuitable for making allowance, when the need arises, for the effect of the boundary field.

We take a molecular model for which the law of *repulsion* $f(r)$ between a pair of molecules is

$$f(r)=Q,\quad (\sigma-\epsilon\leq r<\sigma),$$
$$f(r)=-\phi(r),\quad (r\geqq\sigma).$$

We obtain the elastic sphere model (diameter σ) with the proper field of *attractive* force $\phi(r)$ by making $Q\rightarrow\infty$ and $\epsilon\rightarrow 0$ in a suitable manner. The virial argument starts from the formula *

$$\frac{2\pi N^2}{v}r^2e^{-2j\int_r^\infty f(x)dx}dr$$

for the number of pairs of molecules in the gas whose centres are at a distance between r and $r+dr$. Then for the contribution $\frac{1}{3}\Sigma\Sigma rf(r)$ to the virial we have

$$\tfrac{1}{3}\Sigma\Sigma rf(r)=\frac{2\pi N^2}{3v}\int_0^\infty r^3f(r)e^{-2j\int_r^\infty f(x)dx}dr. \quad . \quad (21)$$

We split this integral up into the two ranges $(\sigma-\epsilon, \sigma)$ and (σ, ∞). In the former we can replace r^3 by σ^3 since eventually $\epsilon\rightarrow 0$. On evaluating $\int_r^\infty f(x)dx$ we get

$$\tfrac{1}{3}\Sigma\Sigma rf(r)=\frac{2\pi N^2\sigma^3}{3v}e^{2j\Pi(\sigma)}\int_{\sigma-\epsilon}^{\sigma}Qe^{-2jQ(\sigma-r)}dr$$
$$-\frac{2\pi N^2}{3v}\int_\sigma^\infty r^3\phi(r)e^{2j\Pi(r)}dr.$$

The first integral can be evaluated; it is

$$\frac{1}{2j}(1-e^{-2jQ\epsilon}).$$

If therefore we make $Q\rightarrow\infty$ and $\epsilon\rightarrow 0$ in such a way that $Q\epsilon\rightarrow\infty$ we may replace the first integral by $1/2j$, which must be its value appropriate to elastic spheres. We can write the second integral in the form

$$-\int_0^\infty r^3\Pi'(r)e^{2j\Pi(r)}dr$$

with our previous conventions for $\Pi(r)$. This can be integrated by parts in the form

$$-\left[\frac{r^3}{2j}(e^{2j\Pi(r)})-1\right]_0^\infty+\frac{3}{2j}\int_0^\infty r^2(e^{2j\Pi(r)}-1)dr,$$

and the integrated part vanishes at both limits. Hence

$$\tfrac{1}{3}\Sigma\Sigma rf(r)=\frac{2\pi N^2\sigma^3}{6jv}e^{2j\Pi(\sigma)}-\frac{2\pi N^2}{2jv}\int_0^\infty r^2(e^{2j\Pi(r)}-1)dr.$$

The complete virial equation is

$$pv=NkT+\tfrac{1}{3}\Sigma\Sigma rf(r),$$

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* Jeans, *loc. cit.* p. 132.

so that in this case, with our previous notation,

$$pv=\mathrm{N}k\mathrm{T}+\frac{1}{v}\left\{\mathrm{N}k\mathrm{T}be^{2j\Pi(\sigma)}-\frac{\mathrm{N}^2\chi(0)}{\nu}\right\}+\mathrm{O}\left(\frac{1}{v^2}\right), \quad (22)$$

which confirms equations (19) and (20). This result is in agreement with Keesom's *, obtained by yet another independent method—the calculation of the entropy.

§ (11). *Particular molecular models.*—The molecular models which are of interest are those in which the attraction (1) varies as the inverse sth power of the distance, $\phi(r)=\alpha r^{-s}$, and (2) is constant over a certain range and zero outside that range, $\phi(r)=\mathrm{A}$, $(\sigma\leq r\leq d)$; $\phi(r)=0$, $(r>d)$. The latter may be regarded as the natural successor of the model originally proposed by Young in his theory of capillary forces. In the first model it is essential for convergence to take $s>4$; the physical meaning of this restriction has already been commented on in § 5.

(i.) *The inverse s^{th}-power law.*—If we take $\phi(r)=\alpha r^{-s}$ we have

$$\left.\begin{aligned}\Pi(r)&=\frac{\alpha r^{1-s}}{s-1},\ (r>\sigma),\\ &=\frac{\alpha\sigma^{1-s}}{s-1},\ (r\leq\sigma).\end{aligned}\right\}\quad .\ .\ .\ .\ .\quad (23)$$

For the second virial coefficient B we combine (19) and (20), expand $e^{2j\Pi(r)}$, and integrate term by term. We obtain after reduction

$$\mathrm{B}=\mathrm{N}k\mathrm{T}b\left\{1-3\sum_{n=1}^{\infty}\frac{(2j\Pi(\sigma))^n}{n\,!\,\{n(s-1)-3\}}\right\}, \quad .\quad (24)$$

where $b=\frac{2}{3}\pi\mathrm{N}\sigma^3$, its classical meaning.

(ii.) *Young's model.*—In this case we have

$$\left.\begin{aligned}\Pi(r)&=0, && (r\overline{>}d),\\ &=\mathrm{A}(d-r), && (d\overline{>}r\overline{>}\sigma),\\ &=\mathrm{A}(d-\sigma), && (\sigma\overline{>}r).\end{aligned}\right\}.\quad .\ .\quad (25)$$

The integral for $\chi(0)$ can be evaluated in finite terms by integration by parts. We obtain after reduction,

$$\chi(0)=\frac{2\pi\nu}{2j}\left\{\left(\frac{1}{3}\sigma^3+\frac{\sigma^2}{2j\mathrm{A}}+\frac{2\sigma}{(2j\mathrm{A})^2}+\frac{2}{(2j\mathrm{A})^3}\right)e^{2j\mathrm{A}(d-\sigma)}\right.$$
$$\left.-\left(\frac{1}{3}d^3+\frac{d^2}{2j\mathrm{A}}+\frac{2d}{(2j\mathrm{A})^2}+\frac{2}{(2j\mathrm{A})^3}\right)\right\}.\quad (26)$$

* *Loc. cit.* p. 264.

Equation (26) is suitable for use in computations for low temperatures. The expanded form for $\chi(0)$ analogous to (24) is suitable for use with high temperatures and is more immediately intelligible than (26). This form is

$$\chi(0)=2\pi\nu\Pi(\sigma)\sum_{n=1}^{\infty}\frac{(2j\Pi(\sigma))^{n-1}}{n\,!}\times\left\{\frac{1}{3}\sigma^3+\frac{(d-\sigma)d^2}{n+1}-\frac{2(d-\sigma)^2d}{n+2}+\frac{(d-\sigma)^3}{n+3}\right\}. \quad (27)$$

and the corresponding form of the second virial coefficient is

$$\mathrm{B}=\mathrm{N}k\mathrm{T}b-2\pi\mathrm{N}^2\Pi(\sigma)\sum_{n=1}^{\infty}\frac{(2j\Pi(\sigma))^{n-1}}{n\,!}\times\left\{\frac{(d-\sigma)d^2}{n+1}-\frac{2(d-\sigma)^2d}{n+2}+\frac{(d-\sigma)^3}{n+3}\right\}. \quad (28)$$

XCII. *The Reflexion of X-Rays from Imperfect Crystals. By* C. G. Darwin, *Fellow and Lecturer of Christ's College, Cambridge* [*].

1. *Introduction.*

THE recent work of Bragg, James, and Bosanquet [†], on the reflexion of X-rays from rock-salt crystals is of extreme importance in that it promises more directly than any other method to supply information about the actual positions which the electrons occupy in the atom. The method consists in a study of the intensity with which the various faces of the crystal reflect a given wave-length, and is based on the theoretical formulæ given by the present writer [‡]. These formulæ showed that such experiments should determine a certain quantity, which is, roughly speaking, the amplitude of the wave scattered by all the electrons in a single atom in the direction of the reflected beam. A study of the various faces of a crystal gives this amplitude as a function of the angle of scattering, and from that the positions of the electrons can be inferred—with this second half of the problem I shall not be here concerned. But the deduction of the amplitude from the experiments encountered certain peculiar difficulties; for the absorption

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[*] Communicated by the Author.

[†] Bragg, James, and Bosanquet, Phil. Mag. vol. xli. p. 309, and vol. xlii. p. 1 (1921).

[‡] Darwin, Phil. Mag. vol. xxvii. p. 315 and p. 675 (1914).

coefficient of the crystal is involved in the formula, and there were indications that the actual absorption was a good deal stronger than usual. This was especially the case in the reflexions at small angles, and these small angles are particularly important, for by them is tested the truth of the hypothesis that in rock-salt the sodium atoms have passed one electron over to the chlorine. The difficulty was overcome—at any rate, partially—by finding the actual absorption coefficients for the various directions in the crystal, by a study of the reflexions of the internal planes of a set of plates of rock-salt. But even this method has an unsatisfactory feature; for it was only possible to arrive at a definite result by rejecting the observations from certain of the plates. It is true that the discrepancy was explained by the fact that these had had much rougher treatment than the rest, but still it suggests a certain measure of doubt as to the soundness of the method, or at any rate the necessity for an inquiry into it. It appeared to me therefore to be worth while to re-examine theoretically the reflexion from crystals in general, in the hope of clearing up the difficulties, and also in the hope that theory would indicate some way of obviating them. The whole point evidently lies in the imperfections of the crystals, and this introduces many complications. I am afraid I have not succeeded in welding the parts of the argument rigorously together, but in spite of certain gaps in the theory it seems unlikely that there is serious error in the general views to which it leads. The work has been rather heavy, but the trouble will have been justified, if it helps in determining the positions of the electrons in the atom, one of the supremely important problems in the present condition of physics.

There will be frequent occasion to refer to the two papers of Bragg, James, and Bosanquet [*]. When mentioning them in the text, I shall, for short, use only the name of the first of the authors. The papers themselves will be called B.J.B. i. and B.J.B. ii. Similarly, my own former papers [†] will be denoted D. i. and D. ii.

2. *Previous Theories.*

The theory of the reflexion of X-rays by crystals was discussed by the present writer in the papers D. i. and D. ii. In D. i. it was assumed that each atom scattered X-rays just as though it was alone, and the solution of this interference

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[*] *Locc. citt.*

[†] *Locc. citt.*

problem led to a formula for the intensity of reflexion. The experimental arrangements to which the calculations were adapted were those in vogue at that time—that is, with crystal fixed during each observation. This was the arrangement used in the experiments of H. G. J. Moseley with the present writer[*], and it was to them that the theoretical calculations were applied. In the course of those experiments a single, but a fairly good, measure was made of the absolute intensity of the reflexion of "white X-rays" and also the curve of reflexion against angle was found. By means of a quadrature it was therefore possible to measure the effect of a single atom, and the result was of the right order for the number of electrons anticipated. Yet it was apparent that the theory was defective, for it was calculated that the diffraction pattern of the reflexion could at most be a few seconds across, and that even if all the available radiation in this breadth were reflected the total would still be far short of the observed amount.

Now, if the reflexion was perfect over any region, it could not be legitimate to treat of the atoms as all scattering independently. In D. ii. therefore the mutual influence of the successive planes was included. It was found that over a breadth of a few seconds the reflexion was perfect, and that in this region the ordinary absorption of the rays by the crystal was swamped by a far more powerful special *extinction.* These principles led to a modified reflexion formula, but one which could explain the magnitude of the reflexion no better than the old. A way was found out of the difficulty by supposing the crystal to be a conglomerate of small blocks of perfect crystal all orientated approximately in the same direction, for such a conglomerate would reflect the radiation at many of its blocks, internal as well as external, and this would much increase the total amount reflected. No attempt was made to treat the problem at all fully, but a general line of argument suggested that the effect would be approximately to reinstate the formula of D. i. without the objections that had before attached to it.

All the calculations of these papers were based on experiments in which the crystal was fixed. A. H. Compton[†] carried out a somewhat similar process quite independently, but based it on the experimental arrangement which has, in fact, proved more convenient in the study of monochromatic

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[*] Moseley and Darwin, Phil. Mag. vol. xxvi. p. 1024 (1913).

[†] Compton, "The Intensity of X-Ray Reflexion," etc., Phys. Rev. vol. ix. p. 29 (1917).

radiation—that in which the crystal turns during the experiment with a constant angular velocity, so as to integrate the effect of the crystal. His results were substantially the same as those of the present writer, though naturally in a form more convenient for comparison with recent experiments. From a mathematical point of view his method has the advantage that he had no need to consider Fresnel integrals, whereas in my method they were necessary in order to secure convergence. I think the identity of results depends on the fact that if an integral nearly converges, and is made to converge by the introduction of a slight convergency factor, then the consequent value is independent of the form of that factor. My factor was the Fresnel term, Compton made his expression converge by cutting it off at the end. As the present paper deals only with small crystals, the case will be analogous to Compton's, the convergence will be assured, and therefore no use will be made of the Fresnel terms.

The same reflexion formula is worked out in B.J.B. i. It is designed to meet the exact requirements of the work, and, though implicitly using the Fresnel integrals, it is free from much of the mathematical complication of the earlier derivations.

3. *General Exposition of the Problem.*

The imperfection of crystals may take either of two forms, warping or cracking. Either the atoms may be arranged on surfaces which are not quite flat, or else they may be arranged in blocks, each block a perfect crystal, but adjacent blocks not accurately fitted together. An examination of the surfaces of rock-salt crystals suggests that the first is probably more the nature of its imperfection, but the second is much more tractable to mathematics and so has been adopted here.

The whole question turns on the phenomenon of extinction, which may be roughly described as the diminution in the reflected beam due to the fact that when one part of a crystal has reflected some of the radiation, there is less for the parts behind it to reflect. In Bragg's work observation was made on the total ionization as the crystal turns through the reflecting angle. Now, at each instant of the rotation there will be a different amount reflected and therefore a different extinction, and consequently it will not suffice to treat of the mean effect of extinction, without first determining it at every setting of the crystal. As will be seen, this complicates the mathematics of the problem considerably.

With regard to the extinction itself it is found that it exerts two effects, which may be called primary and secondary. The primary extinction consists in the reduction of the beam reflected from a *perfect* crystal, owing to the defect in the radiation which reaches its lower layers. As shown in D. ii. it may be deduced by considering the multiple reflexions between the planes of the crystal, and for a deep crystal it leads to perfect reflexion in a region near the reflecting angle. At first sight this is a little paradoxical, but it is easy to see that the simpler formula, which neglects extinction, gives an amount reflected greater than the amount of the incident beam.

The secondary extinction is due to the reduction in intensity of the transmitted beam on emerging from the lower side of a small crystal in which some reflexion has taken place. Its effect is practically to increase the absorption coefficient of the crystal by an amount that can be calculated from the amount of the reflexion. The methods used in B.J.B. ii. remove the secondary extinction, but are without influence on the primary. In fact, it will appear that no experiments of the present type can possibly remove it; indeed, to do so would require the measurement of the actual sizes of the small blocks of perfect crystal. This is a serious difficulty in the problem of determining with certainty the positions of the electrons in the atom; but it should be said that it seems probable that in rock-salt the secondary extinction is far more important than the primary: for, if the imperfection is due to warping rather than cracking, there will be very little primary extinction (which depends on the depths of the perfect crystals), whereas the secondary extinction will be as effective as ever.

A confusing circumstance of the problem has lain in the different physical dimensions of the quantities that occur. For example, it is natural to measure the incident beam by its intensity, erg.cm.$^{-2}$sec.$^{-1}$, whereas the *whole* reflexion is required, and this is of dimensions erg.sec.$^{-1}$. This type of difficulty is illustrated in Bragg's formulæ, which involve a superficially irrelevant angular velocity. I have found it very helpful to adopt the terminology of dimensions for the various quantities occurring. Thus we shall denote the whole ionization produced in the electroscope in a given time as *energy*. Then, following the dynamical usage, *power* will signify energy per time. *Intensity* will be power per area, and *amplitude* will be the square root of intensity. In the example above we should thus speak of the "reflected power." This necessitates a slight alteration from Bragg's terminology. He calls a certain quantity (of zero dimensions) the "reflecting power." To avoid confusion we shall here call it the "integrated reflexion."

The course of the paper is as follows:—

§ 4 treats of the reflexion from a small perfect crystal of any shape and belonging to any of the crystal classes. In § 5 there is found the reflexion from a conglomerate composed of a large number of small crystals orientated nearly in the same direction. In both these sections the crystals are supposed so thin that absorption and extinction are negligible. In § 6 there is a discussion of extinction. In § 7 all the results are combined so as to give the reflexion formula for a deep conglomerate, and in § 8 the same processes are applied to reflexion through a plate—the method of B.J.B. ii. In § 9 there is a short discussion of the rather few experimental results by which the theory can be tested. For the sake of completeness, the formula for reflexion from a powder of crystals is worked out in § 10. The paper concludes with a short general discussion and a summary.

4. *Reflexion from a Small Perfect Crystal.*

We shall first consider the reflexion from a single perfect crystal which is so small that absorption and extinction may be completely neglected. Apart from this condition there is no restriction on its size or shape, and it may belong to any of the crystal classes. Let it be divided into its fundamental lattice. Call the group of atoms in each element of the lattice a molecule. We are not here concerned with symmetry, and there is a certain amount of arbitrariness about the choice of lattice and molecule. For example, in rock-salt it is indifferent whether we take the face-centred cubic lattice, with molecules composed of a sodium atom and one of its chlorine neighbours, or the cubic lattice, containing four atoms of each kind. According to the choice the answer will take a different form, but it is an elementary matter to reconcile the difference.

Take an origin in the crystal, and draw the z axis perpendicular to the planes of which the reflexion is to be studied. Let xz be the plane of incidence of the rays, and let the positive directions of x and z be away from the source. The three primitive translations of the lattice may then be taken as a_x, a_y, a; $b_x, b_y, 0$; $c_x, c_y, 0$. The determinant of the translations is the volume occupied by the molecule and this is $1/\mathrm{N}$, where N is the number of molecules in a cubic centimetre. If an incident beam with amplitude $\mathrm{A}e^{ikct}$ falls on the molecule, let the amplitude of the scattered beam at distance r be $f\mathrm{A}e^{ik(ct-r)}/r$. Here f is of the dimensions of a length, and, apart from the fact that it applies to molecules instead of atoms, is the same as Bragg's $(e^2/mc^2)\,\mathrm{F}$. It will depend on the orientation of the incident and scattered rays and on the wave-length. It will also vary from one molecule to another, according to the chance positions of the electrons, both on account of heat vibration and of the internal motions of the atoms.

Let the incident beam come from an anti-cathode at distance R, and let its amplitude at the crystal be A and its glancing angle of incidence be ζ. Consider the beam scattered to a direction with glancing angle χ and azimuthal angle ψ measured about Oz. Then the source is at $-\mathrm{R}\cos\zeta,\ 0,\ -\mathrm{R}\sin\zeta$, and the point of observation at $r\cos\chi\cos\psi,\ r\cos\chi\sin\psi,\ -r\sin\chi$. The position of a molecule is

$$\left.\begin{aligned} x &= \alpha a_x+\beta b_x+\gamma c_x \\ y &= \alpha a_y+\beta b_y+\gamma c_y \\ z &= \alpha a \end{aligned}\right\}, \qquad \ldots\ldots \quad (4{\cdot}1)$$

where α, β, γ are three integers. For an incident beam $\mathrm{A}e^{ik(ct-\mathrm{R})}$ the wave scattered by this molecule is

$$\mathrm{A}(f_{\alpha\beta\gamma}/r)\exp ik(ct-\mathrm{R}_{\alpha\beta\gamma}-r_{\alpha\beta\gamma}). \qquad \ldots \quad (4{\cdot}2)$$

Expanding $\mathrm{R}_{\alpha\beta\gamma}$ and $r_{\alpha\beta\gamma}$, the amplitude of the total scattered wave is

$$(\mathrm{A}/r)e^{ik(ct-\mathrm{R}-r)}\sum_{\alpha\beta\gamma} f_{\alpha\beta\gamma}\exp ik[x(\cos\chi\cos\psi-\cos\zeta) \\ +y\cos\chi\sin\psi-z(\sin\chi+\sin\zeta)].$$

To find the intensity multiply by the conjugate imaginary. If $\mathrm{J}=\mathrm{A}^2$ is the intensity of the incident beam, this gives

$$(\mathrm{J}/r^2)\sum_{\alpha\beta\gamma}\sum_{\alpha'\beta'\gamma'} f_{\alpha\beta\gamma}f'_{\alpha'\beta'\gamma'}\exp ik[(x-x')(\cos\chi\cos\psi-\cos\zeta) \\ +(y-y')\cos\chi\sin\psi-(z-z')(\sin\chi+\sin\zeta)]\ \ldots., \quad (4{\cdot}3)$$

where $x'=\alpha' a_x+\beta' b_x+\gamma' c_x$, etc. f and its conjugate f' will vary from one molecule to another. We must take the mean of (4·3), allowing for the chance variations of f. This will be done by a double averaging of all possible values of α, β, γ and α', β', γ', and as all pairs of molecules occur in the sum this is the same as taking the mean of f and squaring its modulus. This quantity will be denoted by f^2; it is different from the mean intensity scattered by a single molecule*.

Suppose that the crystal is set so that ζ is near θ, where θ is given by the equation $ka \sin\theta = n\pi$, which determines reflexion in the nth order. For angles far from this the reflexion is insignificant, so we may put

$$\zeta = \theta + u, \qquad \chi = \theta + v,$$

and treat u, v, ψ as small. This approximation excludes all the other reflexions from consideration. The reflected intensity is then

$$(\mathrm{J}/r^2) f^2 \sum_{\alpha\beta\gamma} \sum_{\alpha'\beta'\gamma'} \exp ik\{(x-x')(u-v)\sin\theta + (y-y')\psi\cos\theta - (z-z')(u+v)\cos\theta\}. \quad . \quad . \quad (4{\cdot}4)$$

From this a factor $\exp - 2ik(z-z')\sin\theta$ has been rejected, as it is equal to unity. Now on account of the smallness of u, v, ψ the exponential terms only vary slowly with α, β, γ, and so it will be legitimate to replace the summations by integrations. The number of terms contained in a volume $d\mathrm{V}$ is $\mathrm{N}d\mathrm{V}$ and so the intensity becomes

$$(\mathrm{J}/r^2)\mathrm{N}^2 f^2 \int^{(6)} d\mathrm{V}\, d\mathrm{V}' \exp ik\{\mathrm{F}(x-x') + \mathrm{G}(y-y') + \mathrm{H}(z-z')\}, \quad . \quad . \quad . \quad (4{\cdot}5)$$

where $\mathrm{F} = (u-v)\sin\theta$, $\mathrm{G} = \psi\cos\theta$, $\mathrm{H} = -(u+v)\cos\theta$, and the volume integrations are each taken over the whole crystal.

We shall now suppose that the crystal is put through one of Bragg's experiments. An instrument is placed so that it can catch all the reflected radiation. The element of area at r is $r^2 \cos\chi\, d\chi\, d\psi$ or $r^2 \cos\theta\, dv\, d\psi$, and so (4·5) must be multiplied by this and integrated over all values of v and ψ. Further, the crystal is made to rotate with angular velocity ω about the y axis, and the total energy E received by the instrument is measured. This is equivalent to an integration $\int du/\omega$ taken over all values of u. Then

$$\mathrm{E} = \int_{-\infty}^{\infty} du/\omega \iint_{-\infty}^{\infty} r^2 \cos\theta\, dv\, d\psi \times (4{\cdot}5).$$

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* See Bragg, James, and Bosanquet, *Zeitschrift für Physik,* vol. viii. p. 77 (1921).

To perform the integrations change variables from u, v, ψ to F, G, H; the latter will all go from $-\infty$ to ∞, and

$$du\,dv\,d\psi = d\mathrm{F}\,d\mathrm{G}\,d\mathrm{H}\ \mathrm{cosec}\ 2\theta\ \sec\theta,$$

and so

$$\mathrm{E}\omega/\mathrm{J} = \mathrm{N}^2 f^2\ \mathrm{cosec}\ 2\theta \iiint_{-\infty}^{\infty} d\mathrm{F}\,d\mathrm{G}\,d\mathrm{H} \int^{(6)} d\mathrm{V}\,d\mathrm{V}'$$

$$\exp ik\{\mathrm{F}(x-x') + \mathrm{G}(y-y') + \mathrm{H}(z-z')\}. \quad . \quad (4{\cdot}6)$$

This expression can be evaluated by an inversion of the order of integration; I shall not attempt to justify the process rigorously. First, take the F, G, H integrations between the large limits $\pm\mathrm{F}_\infty$, etc. Then

$$\mathrm{E}\omega/\mathrm{J} = \mathrm{N}^2 f^2\ \mathrm{cosec}\ 2\theta\,(2/k)^3\ \mathrm{Lt} \int^{(6)} d\mathrm{V}\,d\mathrm{V}'$$

$$\frac{\sin k\mathrm{F}_\infty(x-x')}{x-x'}\ \frac{\sin k\mathrm{G}_\infty(y-y')}{y-y'}\ \frac{\sin k\mathrm{H}_\infty(z-z')}{z-z'}.$$

Now in the x' integration, which is to follow next, the presence of F_∞ implies that the only important part is near $x'=x$. Similarly, for y' and z'. Hence it will be valid to take these three integrations over all space instead of only over the crystal, for the parts outside will contribute nothing. We now have

$$\int_{-\infty}^{\infty} \frac{\sin k\mathrm{F}_\infty(x-x')}{x-x'}\,dx' = \pi, \text{ etc.}$$

The final three integrations then simply yield

$$\mathrm{E}\omega/\mathrm{J} = \mathrm{N}^2 f^2\ \mathrm{cosec}\ 2\theta\,(2/k)^3\,.\,\pi^3\,.\,\mathrm{V}.$$

Now $2\pi/k$ is the wave-length λ. Also we shall adopt the notation of B.J.B. ii. and write

$$\mathrm{Q} = \mathrm{N}^2 f^2 \lambda^3\ \mathrm{cosec}\ 2\theta. \quad . \quad . \quad . \quad . \quad (4{\cdot}7)$$

Then

$$\mathrm{E}\omega/\mathrm{J} = \mathrm{QV}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4{\cdot}8)$$

Q is of the dimensions of the reciprocal of a length. This equation is the same as B.J.B. i. p. 326 (4). A little care is needed in considering it, because its physical dimensions are different from those of other equations which will occur later, though it is similar to them in appearance.

The factor Q will include the special peculiarities of the crystal, such as the weak (1, 1, 1) reflexion of rock-salt.

The averaging process will introduce the temperature factor $e^{-B\sin^2\theta}$ and, if desired, the meaning of this may be modified so as to include the relative motions of the atoms in the molecule. There will also be the usual polarization factor $\frac{1}{2}(1+\cos^2 2\theta)$. If these are put in explicitly

$$Q=N^2f^2\lambda^3 \operatorname{cosec} 2\theta\, e^{-B\sin^2\theta}\tfrac{1}{2}(1+\cos^2 2\theta). \quad . \quad (4\cdot9)$$

Here f will represent the mean scattering in the equatorial plane of the emergent spherical wave from a molecule; it is the right quantity for determining the distribution of the electrons. In this paper we shall only be concerned in the deduction of the value of Q and nothing further will be said about the other half of the problem.

The result of this section has been proved without allowance for the fact that the incident waves are really spherical and that the Fresnel zones are exceedingly small in X-ray work. It is easy to carry out the whole process, retaining the squares of x, y, z; but the formulæ are much more cumbrous. As they lead to precisely the same result, it is not necessary to give them.

5. *Reflexion from a Conglomerate.*

The next problem to be considered is the reflexion from a small imperfect crystal. It is supposed to be made up of a number of perfect crystals differing slightly in their orientations, and the whole is to be so thin that extinction and absorption are negligible. We shall describe it as a *conglomerate* and the component perfect crystals as *blocks.* Suppose that such a conglomerate is put through the same experiment as in § 4. At every point of the observing instrument the intensity will be the sum of the intensities from the separate blocks. Hence the integrated energy will be given by (4·8), where now V is the volume of the whole conglomerate. But this is not enough; it is also necessary to find the actual reflexion when the crystal is fixed at any angle of incidence—a much more difficult matter. However, Bragg's experiments showed that there was reflexion for settings of the crystal differing by as much as a degree, which is very much larger than the breadth of the diffraction pattern of a single block, and this fact makes it possible to approximate. We defer the discussion of the size of blocks required for the approximation to be valid.

Consider a block of volume W which has normal l, m, -1 (it is convenient to take it in the negative direction), where

l, m are small and are measured with reference to some standard direction in the conglomerate, not necessarily the mean direction of the blocks. The intensity of the beam reflected by a single block is then given by (4·5) provided that $u-l$ is put for u, $v+l$ for v, and $\psi-2m\tan\theta$ for ψ. To specify the distribution of the blocks let

$$\mathrm{VF}(\mathrm{W}, l, m)d\mathrm{W}\,dl\,dm \quad . \quad . \quad . \quad . \quad (5{\cdot}1)$$

be the number of blocks in the volume V of the conglomerate which are themselves of volumes between W and $\mathrm{W}+d\mathrm{W}$ and have normals between l, m and $l+dl$, $m+dm$. It follows that

$$\int d\mathrm{W}\iint_{-\infty}^{\infty} dl\,dm\,\mathrm{WF}(\mathrm{W}, l, m)=1. \quad . \quad . \quad . \quad (5{\cdot}2)$$

The intensity of reflexion in the direction v, ψ is therefore obtained by taking (4·5) for a volume W (modified as above), multiplying it by (5·1) and integrating over all values of W, l, m that occur. To obtain the reflected power we multiply by $r^2\cos\theta\,dv\,d\psi$ and integrate over all values of v, ψ. The result is

$$\mathrm{JN}^2f^2\cos\theta\,.\,\mathrm{V}\iint_{-\infty}^{\infty} dv\,d\psi\int^{(3)}\mathrm{F}(\mathrm{W}, l, m)d\mathrm{W}\,dl\,dm\int_{\mathrm{W}}^{(6)} d\mathrm{V}\,d\mathrm{V}'$$

$$\exp ik\{(x-x')(u-v-2l)\sin\theta+(y-y')(\psi\cos\theta-2m\sin\theta)$$

$$-(z-z')(u+v)\cos\theta\}. \quad . \quad . \quad . \quad (5{\cdot}3)$$

This is a function of the angle of incidence, that is of u, and the fact that we are not to integrate for u alters the procedure. We must use the assumption that the diffraction pattern of each block extends over a much narrower angle than the distribution of the blocks. Now, if the shape of the blocks were known, it would be possible to carry out the six last integrations, and, regarding the result as a function of l, the l integrand would then consist of the product of two functions, one of which vanishes except for a narrow peak. It would then be correct to substitute in the rest of the integrand the value of l given by the maximum of the narrow peak—that is, to substitute $\frac{1}{2}(u-v)$ for l in F. We may make the same change, even when the order of integrations is altered so as to do that for l first. The same argument also applies for ψ and m. If l_∞, m_∞ denote quantities which are to be made infinite later, the result of the l and m integrations is

$$\frac{JN^2 f^2 \cos\theta}{k^2 \sin^2\theta} \cdot V \iint dv\, d\psi \int F\left(W, \frac{u-v}{2}, \frac{\psi \cot\theta}{2}\right) dW \int_W^{(6)} dV\, dV'$$

$$\frac{\sin k(x-x')\sin\theta \,.\, 2l_\infty}{x-x'}\,\frac{\sin k(y-y')\sin\theta \,.\, 2m}{y-y'}$$

$$\times \exp - ik(z-z')(u+v)\cos\theta.$$

In this x' has been equated to x and y' to y in all the terms that do not involve l_∞, m_∞. Next integrate for v. With exactly the same argument, we may put $-u$ for v in F, and this makes the integration possible. The result is

$$\frac{JN^2 f^2}{k^3 \sin^2\theta} \cdot 2V \int_{-\infty}^{\infty} d\psi \int F(W, u, \tfrac{1}{2}\psi \cot\theta)\, dW \int_W^{(6)} dV\, dV'$$

$$\frac{\sin k(x-x')\sin\theta \,.\, 2l_\infty}{x-x'}\,\frac{\sin k(y-y')\sin\theta \,.\, 2m_\infty}{y-y'}$$

$$\times \frac{\sin k(z-z')\cos\theta \,.\, v_\infty}{z-z'}.$$

The argument of § 4 now shows that the double volume integration is equal to $\pi^3 W$. Thus the whole effect is

$$JN^2 f^2 \lambda^3 \operatorname{cosec} 2\theta \,.\, V \int dW \int_{-\infty}^{\infty} WF(W, u, m')\, dm'.$$

Let

$$Q \int dW \int dm'\, WF(W, u, m') = G(u). \quad . \quad . \quad (5{\cdot}4)$$

Then, using (4·7), the power reflected is

$$JV\,G(u), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}5)$$

and by (5·2)

$$\int_{-\infty}^{\infty} G(u)\, du = Q. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5{\cdot}6)$$

The relation (5·5) is practically equivalent to saying that the incident beam is reflected by those blocks which are at the proper angle and no others*.

In order to test the validity of the assumptions made in this work, we shall simplify the problem by supposing that all the blocks are rectangular of sides ξ, η, ζ and orientated

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* With a little modification the same argument proves the result deduced in general terms in D. ii, p. 686.

according to the error law. Let σ be the *scatter* of the blocks—that is, the departure of mean square of the normal of a block from that of the conglomerate. Then for (5·1) we must write

$$\frac{\mathrm{V}}{\xi\eta\zeta}\frac{\exp-(l^2+m^2)/2\sigma^2}{2\pi\sigma^2}. \quad . \quad . \quad . \quad . \qquad (5·7)$$

It is now possible, though still tedious, to work out (5·3) down to the last integration, which involves an error function. Approximating for this when u is small we find

$$\mathrm{JVQ}\frac{e^{-u^2/2\sigma^2}}{\sqrt{2\pi}\sigma}\left\{1-\frac{1-u^2/2\sigma^2}{\sqrt{2\pi}\sigma\,.\,k\sin\theta\,.\,\xi}\right\}, \quad . \qquad (5·8)$$

as the expression corresponding to (5·5); so the validity of (5·5) depends on neglecting the second term in the bracket. Thus for a first-order reflexion a/ξ must be small compared to σ. In Bragg's experiments σ was of the order of 1°; so to get an accuracy of 1 per cent. ξ/a must be of the order of 10^4. For spectra of higher orders the conditions are less exacting.

From the general appearance of the work one may hazard a guess that the approximation will be true over a much wider range of values, and would cover the case of a crystal imperfect by warping. It is, of course, possible always to define a function $\mathrm{G}(u)$ so as to satisfy (5·5) and it will probably be always true that $\int_{-\infty}^{\infty}\mathrm{G}(u)\,du=\mathrm{Q}$; but the important point is that $\mathrm{G}(u)/\mathrm{Q}$ should depend only on the structure of the conglomerate, for only so will it be possible to pass from reflexion of one order to one of another and from one set of crystal planes to another.

6. *Extinction.*

The calculations have so far dealt with crystals which are so thin that absorption and extinction can be neglected. It is now necessary to inquire to what extent this is justified. In D. ii. a study was made of the reflexion from an infinitely deep perfect crystal, and it was shown that the reflexion is practically perfect when the glancing angle differs from θ by less than $q/ka\cos\theta$, where $q=\mathrm{N}f\lambda a\operatorname{cosec}\theta$ is the coefficient of reflexion for a single plane (a quantity of zero dimensions); while on either side of this band it falls off rather rapidly to zero. Inside the crystal the transmitted beam was found to be extinguished at a rate depending on the exact angle, the greatest factor being $e^{-2qz/a}$ at the central point. Now if we take the numerical value which q would have in Bragg's experiments, using rhodium K_α rays and the (1, 0, 0) planes of rock-salt, we find that $q=2\times10^{-4}$ and $2q/a=14000$. The ordinary absorption, measured by depth, is $\mu \operatorname{cosec}\theta=100$; so it is quite clear that extinction will be of far greater importance. Moreover, if we suppose the crystal only a thousand layers thick we have $2qz/a=2q\times1000=0{\cdot}4$, so in even quite a thin layer the extinction may be expected to become considerable, and its influence must be examined. We shall see that it cannot be neglected, but that there is a considerable modification in the formulæ.

In D. ii. the phenomenon was studied for an infinitely broad and infinitely deep crystal. The latter condition is to be altered, but to give up the infinite breadth would lead to great difficulty and we shall therefore retain this condition. It requires, however, an alteration in the type of observation, for an infinite plane will always reflect the rays from *some* point of its surface and so there will be no definite reflecting position. We therefore take a fixed crystal and find the total power reflected for a point source.

Take a crystal composed of m planes, and first consider its effect on plane waves. The equations of D. ii. p. 678 are applicable. They deal with the multiple reflexions in the successive planes of the crystal, allowing, of course, for their phase relations. The difference equations connecting T_r, the amplitude of the transmitted wave at the rth plane, with S_r, that of the reflected, take the form *

$$\left.\begin{aligned} S_r &= -iq\,T_r + (-)^n(1-h-ika\cos\theta\,.\,u)S_{r+1} \\ T_{r+1} &= (-)^n(1-h-ika\cos\theta\,.\,u)T_r - iq\,S_{r+1} \end{aligned}\right\}, \qquad (6{\cdot}1)$$

where $h=\frac{1}{2}\mu a\operatorname{cosec}\theta$ is the absorption factor for amplitude. The form of the solution will differ from that in D. ii., as the

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* It has not been possible to retain completely the same notation as D. ii. The following are the chief differences:—

D. ii.	θ	ϕ	v
Here	$\theta+u$	θ	$ka\cos\theta\,.\,u$.

I am afraid that in D. ii. ϵ was used in two senses; on p. 679 it has the same meaning as here, but on p. 681 it is the same as u here.

end condition now is $S_m=0$. The solution is found to be

$$\left.\begin{aligned} S_0 &= -iq\,T_0/(h+ika\cos\theta\,.\,u+\epsilon\coth m\epsilon) \\ T_m &= \epsilon\,\mathrm{cosech}\,m\epsilon\,.\,T_0/(h+ika\cos\theta\,.\,u+\epsilon\coth m\epsilon) \end{aligned}\right\}, \quad (6{\cdot}2)$$

where $$\epsilon^2=q^2+(h+ika\cos\theta\,.\,u)^2. \quad . \quad . \quad . \quad . \quad (6{\cdot}3)$$

Now, as we saw, h is very much smaller than q. If we neglect it altogether we have

$$\left.\begin{aligned} &\epsilon=\sqrt{q^2-(ka\cos\theta\,.\,u)^2} \quad \text{for} \quad |u|<q/ka\cos\theta \\ \text{and} \quad &\epsilon=i\sqrt{(ka\cos\theta\,.\,u)^2-q^2} \quad \text{for} \quad |u|>q/ka\cos\theta \end{aligned}\right\}. \quad (6{\cdot}4)$$

It is then easy to verify that for all values of u

$$|T_m|^2+|S_0|^2=|T_0|^2.$$

Further, if h is not quite zero, it may be verified that to a first approximation

$$|T_m|^2+|S_0|^2=|T_0|^2(1-2mh). \quad . \quad . \quad . \quad (6{\cdot}5)$$

Thus we can always calculate the intensity of the transmitted beam by reducing the incident by an amount corresponding to ordinary absorption and subtracting from it the intensity reflected. This will play an important part in the next section, as it gives rise to the secondary extinction.

Now, consider the reflected beam coming from a point source. Following the line of argument of D. ii., we may resolve the spherical wave into plane, and the whole reflexion is given by integrating the plane wave formula over all values of u. The exact form of the answer involves such matters as the length of the slit in the observing instrument, but here it will suffice to find a quantity that is proportional to it. This is

$$\int_{-\infty}^{\infty}|S_0|^2\,du=q^2|T_0|^2\int_{-\infty}^{\infty}du/|h+ika\cos\theta\,.\,u+\epsilon\coth m\epsilon|^2. \quad . \quad . \quad . \quad (6{\cdot}6)$$

The evaluation of the integral seems to be impossible in general, but our object can be achieved by taking advantage of the smallness of h and using (6·4). But there is a complication; for unless h actually vanishes, ϵ will have a small real part in the outer region, and therefore if m is large enough $\coth m\epsilon$ will tend to unity. This will bring the denominator to the form it had in D. ii., viz.:

$$|\,ika\cos\theta\,.\,u+i\sqrt{(ka\cos\theta\,.\,u)^2-q^2}\,|^2.$$

But if we put $h=0$ before allowing m to become large, the corresponding expression is

$$|\,ika\cos\theta\,.\,u+\sqrt{(ka\cos\theta\,.\,u)^2-q^2}\cot m\sqrt{(ka\cos\theta\,.\,u)^2-q^2}\,|^2.$$

The integral still converges, but to a different value. To avoid this difficulty we must suppose that the crystal is so thin that mh is small—it must be less than about 10^5 layers thick. For such a crystal the real part of ϵ will not matter and we may put $h=0$ and write the relations (6·4) straight into (6·6). In spite of its unpromising appearance the integral can be evaluated and leads to the remarkably simple result *

$$\int_{-\infty}^{\infty}|\,S_0|^2\,du=|\,T_0|^2\frac{q}{ka\cos\theta}\,\pi\tanh mq. \quad . \quad . \quad (6\cdot7)$$

If in this we allow m to become infinite the result is $|\,T_0|^2\,\pi\dfrac{q}{ka\cos\theta}$, whereas the true value from D. ii. should be $|\,T_0|^2\dfrac{8}{3}\dfrac{q}{ka\cos\theta}$; so even in this extreme case the error is only 18 per cent. for taking h zero before putting m infinite. This shows that the approximation may be expected to hold for quite deep crystals with considerable accuracy.

Now take the same problem and work it out on the principles of § 4. It is easily found that

$$S_0=-iq\,T_0\frac{1-\exp-2mika\cos\theta\,.\,u}{2ika\cos\theta\,.\,u},$$

which leads to the result

$$\int_{-\infty}^{\infty}|\,S_0|^2\,du=|\,T_0|^2\frac{q}{ka\cos\theta}\,\pi\,.\,mq. \quad . \quad . \quad (6\cdot8)$$

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[*] This result was first discovered by obtaining an expansion in terms of mq. The complete proof may be constructed as follows. Write the denominator as the product of two conjugate imaginaries and split it into partial fractions. Next express it as a complex integral with argument ϵ.... necessitating a *cut* between $\pm q$ in the ϵ-plane. It may then be proved that the poles of either fraction in the integrand lie entirely on one or other side of the path of integration. Hence the path may be replaced by a circle at infinity which contributes nothing, together with a small circle round $\epsilon=q$ which introduces the hyperbolic tangent.

So we may represent the effect of extinction by introducing a correction factor

$$\frac{\tanh mq}{mq}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\cdot9)$$

and this is quite accurate for crystals not so deep that the ordinary absorption would become important, and remains fairly good even for those much deeper.

Now consider a small block limited in breadth as well as depth and irradiated by plane waves. The multiple internal reflexions will give a complicated system, which will depend on the crystal's shape and will be irregular at its surfaces. But it seems reasonable to represent its effect by calculating the intensity of reflexion as though it were of infinite area, and then selecting from the reflected rays the cross-section which has met the actual crystal. Let d be the mean depth, then V/d is the area. The cross-section of the rays is therefore $(V/d)\sin\theta$, and so the power reflected is

$$|S_0|^2 (V/d)\sin\theta.$$

Then we have

$$E = \int_{-\infty}^{\infty} |S_0|^2 (V/d)\sin\theta\, du/\omega.$$

If we put $|T_0|^2 = J,\ d = ma,\ q^2 = 2Qa^2\cot\theta/\lambda$,

we thus get $$E\omega/J = VQ\tanh mq/mq, \quad . \quad . \quad . \quad (6\cdot10)$$

which shows that on these assumptions the same correction factor is applicable in (4·8) as in (6·8).

Exactly the same process may be applied to the argument of § 5. For though there the crystal was not rotating, yet the distribution of the blocks was such that there was an integration, equivalent in its effects to the u integration here. We may thus say that the reflexion of a conglomerate at angle $(\theta + u)$ is given by

$$JVG(u), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6\cdot11)$$

provided that

$$G(u) = Q'\int dW \int_{-\infty}^{\infty} dm'\, WF(W, u, m'), \quad . \quad (6\cdot12)$$

where $$Q' = Q\tanh mq/mq. \quad . \quad . \quad . \quad . \quad (6\cdot13)$$

In consequence of this (5·6) becomes

$$\int_{-\infty}^{\infty} G(u)\,du = Q'. \quad . \quad . \quad . \quad . \quad . \quad (6\cdot14)$$

The extinction factor is perhaps more properly expressed in terms of the depth of the block, rather than the number of its planes, because this will be roughly the same in all directions and so will give rise to a formula suitable for comparing reflexions of different faces of the crystal. Then the extinction factor is

$$\frac{\tanh\sqrt{2Qd^2\cot\theta/\lambda}}{\sqrt{2Qd^2\cot\theta/\lambda}}$$

$$=1-\frac{2}{3}\frac{Qd^2\cot\theta}{\lambda}+\frac{8}{15}\frac{Q^2d^4\cot^2\theta}{\lambda^2}-\ldots\ldots \quad (6\cdot15)$$

Considering the numerical values in Bragg's experiments, it appears that for a block two thousand layers thick the correction will be about 5 per cent.

Thus we see that a conglomerate of crystals of size d will give rise to a Q modified by the extinction factor (6·15). This modification is the primary extinction, and as we shall see it is untouched by Bragg's method of eliminating extinction. The secondary extinction arises in considering the action of the transmitted beam on the lower blocks. It may be calculated by allowing for the ordinary absorption of the incident beam and in addition subtracting from it the amount of the reflexion. As this last depends on Q′ the secondary extinction will do so too.

7. *Reflexion from a Face.*

Now consider what happens when a beam strikes the face of a thick conglomerate at any angle near the angle of reflexion. Imagine the conglomerate divided into successive layers. In the first layer it will find a few blocks rightly placed, and from each of these a ray will be reflected. In § 6 we saw that extinction would reduce the intensity of the transmitted beam by an amount equal to the intensity of the reflected beam. After traversing the first layer the beam will thus be defective in a few patches, where particular blocks have been able to extinguish it; but in considering the effect of many layers it will be correct to average the intensity after traversing each and so treat it as uniform for the next. To obtain the power transmitted through a single layer, we shall therefore take the power reflected by it, subtract it from the incident and reduce the result by an amount given by the ordinary absorption.

The whole reflexion from a deep crystal results from the multiple reflexions in the successive layers. The multiplicity is of a different type from that of (6·1) because the rays are not now coherent. The problem of these multiple reflexions would be exceedingly difficult if it were treated exactly; for each layer will, on account of diffraction, spread out incident parallel rays into a certain range of angles and so will continually change the angle at which they attack the successive layers. But, if (as assumed in § 5) the crystal is so imperfect that diffraction does not change the direction of the rays to an extent comparable with the scale of variation in the orientations of the blocks, then it will be legitimate to regard the reflected rays as coming plane parallel off the crystal (at an angle exactly 2θ to the incident beam). In consequence of this it will be possible to replace a highly complicated system of integral equations by differential equations of a simple type.

Suppose that a plane incident beam of total power I strikes a deep crystal at angle $\theta+u$ to the face, and let E_u be the total power reflected. Let $I_u(z)$ and $E_u(z)$ be the powers of the incident and reflected beams at a depth z inside the crystal. Suppose that the area of face they strike is B, and consider the effect of a layer of thickness δz. The incident beam has cross-section $B \sin(\theta+u)$ and so its intensity is $I_u(z)/B\sin(\theta+u)$. The power reflected by the volume $B\delta z$ will, by (6·11), be therefore $I_u(z)\,\delta z\, G(u) \operatorname{cosec}(\theta+u)$. The incident beam will lose the same amount through extinction, while through absorption it will lose $I_u(z)\,\delta z\,\mu \operatorname{cosec}(\theta+u)$. In the same way the reflected beam will be partly reflected back again. To treat of it we must regard the conglomerate upside down—that is, for $F(W, l, m)$ in (5·1) we must write $F(W, -l, -m)$ and also for u, $-u$. Thus $G(u)$ will be unaltered in form, and the beam $E_u(z+\delta z)$, which is coming outwards through the layer δz, throws an amount

$$E_u(z+\delta z)\,\delta z\, G(u) \operatorname{cosec}(\theta-u)$$

back into the incident direction. Corresponding to this there is an amount

$$E_u(z+\delta z)\,\delta z\,\{\mu+G(u)\} \operatorname{cosec}(\theta-u)$$

absorbed and extinguished. Balancing up the gains and losses we arrive at a pair of equations,

$$\left.\begin{aligned} \frac{\partial I_u(z)}{\partial z} &= -\frac{\mu+G(u)}{\sin(\theta+u)} I_u(z) + \frac{G(u)}{\sin(\theta-u)} E_u(z) \\ -\frac{\partial E_u(z)}{\partial z} &= -\frac{\mu+G(u)}{\sin(\theta-u)} E_u(z) + \frac{G(u)}{\sin(\theta+u)} I_u(z) \end{aligned}\right\}. \quad (7{\cdot}1)$$

These equations will be true even when the scatter of the blocks varies with the depth in the crystal, but to make progress we shall suppose it constant—that is, $G(u)$ is not a function of z. This makes the equations linear. The end conditions are that $I_u(z)$ and $E_u(z)$ should vanish for infinite z. There is no need to give the solution in detail—E_u the value at the surface is what is required. It is *

$$E_u/I=\frac{\sin(\theta-u)}{\sin\theta\cos u}G(u)\Big/\Big[\mu+G(u) + \surd\{[\mu+G(u)]^2-[G(u)]^2(1-\cot^2\theta\tan^2 u)\}\Big]. \quad . \quad (7{\cdot}2)$$

The first factor represents the influence of having a crystal face that is not the true reflexion plane—whether because the surface is covered by a vicinal face or because it has been badly ground. For the layers into which the crystal was divided were drawn parallel to the actual face, and if this is not the true reflexion face $G(u)$ will be unsymmetrical about $u=0$. Now suppose that the source and point of observation are interchanged—this is the same as observing on the other side of the spectrometer. We must then draw the x axis in the other direction, and so shall obtain a formula involving $-u$ instead of u. But if on this side we take $u'=-u$ we shall have

$$E'_{u'}/I=\frac{\sin(\theta+u')}{\sin\theta\cos u'}G(u')/\{\mu+G(u')+\text{ etc.}\}.$$

Thus if we compare together points where the u of one side is the same as the u' of the other, then clearly

$$E'_u/E_u=\sin(\theta+u)/\sin(\theta-u).$$

In the case of a fairly perfect vicinal face all the settings which give perceptible reflexion will be not far from $u=\alpha$, the inclination of the face, and so the ratio of all pairs of corresponding powers will be nearly $\sin(\theta+\alpha)/\sin(\theta-\alpha)$, and therefore the same will be true of the integrated reflexion. This factor may also be derived by simple consideration of the area of the crystal on which a limited beam would fall in the two cases. The difference of the reflexions was originally observed by Sir W. H. Bragg †, and

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* *Mutatis mutandis* this is substantially the solution obtained by K. W. Lamson, Phys. Rev. vol. xvii. p. 624, by quite a different method. If (7·1) are treated as difference equations his exact form is obtained.

† W. H. Bragg, Phil. Mag. vol. xxvii. p. 888 (1914). At first I thought my explanation was different from his; but through correspondence it became evident that we were only regarding the matter from different points of view. I wish to express my thanks to him for his interest in the matter.

explained by considering the absorption of the emergent beams in the two cases. His argument leads to the same factor. The influence of the vicinal face can be completely eliminated by averaging for both sides, and we shall suppose this done. There is then no need to consider the first factor in (7·2) at all.

Bragg's "reflecting power" (which we are here calling the *integrated reflexion*) was defined by him as $E\omega/I$, where the crystal was turned with angular velocity ω through the reflecting angle and E was the total energy obtained, while I was the power of the incident beam. His I is the same as ours, his E is our $\int_{-\infty}^{\infty} E_u \, du/\omega$. So we have for the integrated reflexion

$$\rho = \int_{-\infty}^{\infty} G(u)\,du \Big/ \left\{ \mu + G(u) + \sqrt{[\mu+G(u)]^2 - [G(u)]^2(1-\cot^2\theta\tan^2 u)} \right\} . \quad (7\cdot3)$$

If $G(u)$ is small compared with μ for every value of u, then neglecting the small terms of the denominator and using (6·4) we have

$$\rho = Q'/2\mu.$$

Apart from the difference between Q' and Q, this is the equation used in B.J.B. i.

If $G(u)$ is not always small enough to justify this approximation, it may still be small enough to admit of expansion in powers of $G(u)/\mu$. Then we have

$$\rho = \frac{1}{2\mu}\int_{-\infty}^{\infty} G(u)\,du - \frac{1}{2\mu^2}\int_{-\infty}^{\infty} G^2(u)\,du + \frac{1}{\mu^3}\int_{-\infty}^{\infty} G^3(u)\left(\tfrac{5}{4} - \cot^2\theta\tan^2 u\right) du.$$

Let

$$\left.\begin{aligned} \int_{-\infty}^{\infty} G^2(u)\,du &= g_2 Q'^2 \\ \int_{-\infty}^{\infty} G^3(u)\,du &= g_3 Q'^3 \end{aligned}\right\} ; \quad . \quad . \quad . \quad . \quad (7\cdot4)$$

then g_2 and g_3 will be constants of the crystal. For most crystals it will be legitimate to neglect the term involving

$\tan^2 u$. Then

$$\rho=\frac{Q'}{2\mu}-g_2\frac{Q'^2}{2\mu^2}+g_3\frac{5\,Q'^3}{4\mu^3}$$

$$=\tfrac{1}{2}Q'\Big/\left\{\mu+g_2Q'+(g_2{}^2-\tfrac{5}{4}g_3)\frac{Q'^2}{\mu}\right\}. \quad . \quad (7\cdot5)$$

If the third term is neglected this is in the form used by Bragg, who calls g_2Q' the "extinction coefficient." If we had considered that every incident and every reflected beam had only a single reflexion, then we should have had instead of (7·2)

$$E_u/I=\tfrac{1}{2}G(u)/\{\mu+G(u)\},$$

and this would lead to the same first two terms in (7·5). This idea has been used by Sir W. H. Bragg *, and it is clear that there will be a wide region of values in which it will be a very good approximation.

It is evident that a knowledge of ρ by itself is not sufficient to determine the value of Q'; but (7·2) suggests that it may be possible to do so by a study of the shape of the reflexion curve. For if we know E_u for all values of u we may solve (7·2) for $G(u)$. If the first factor is omitted, we have

$$G(u)=\frac{2\mu(E_u/I)}{1-2(E_u/I)+(1-\cot^2\theta\tan^2 u)(E_u/I)^2}. \quad (7\cdot6)$$

A quadrature will then lead to Q' by (6·14), and so the secondary extinction is eliminated.

It thus appears theoretically possible to determine Q' from observation on a single face. There is, however, a serious objection to the method. It is not reasonable to suppose that $G(u)$ is really independent of the depth; for grinding or even cleaving must necessarily act differently on the surface-layers and interior, and if G is an unknown function of z, the data are insufficient for a solution. If, in spite of this, the process should be valid, there would still be the difficulty that Q' may differ from Q. The only possibility of determining Q would appear to lie in finding Q' for several crystals, of which the blocks were scattered in various degrees. If then the results all came the same, there would be a presumption that primary extinction was not present. Of two discordant values the greater is to be

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* W. H. Bragg, Phil. Mag. vol. xxvii. p. 881 (1914), and Proc. Lond. Phys. Soc. vol. xxxiii. p. 304 (1921).

preferred, and it would be expected that this greater value would be associated with a greater scattering among the blocks—that is, a broader region of reflexion.

8. *Reflexion through a Plate.*

To overcome the difficulty of the unknown extinction Bragg sent X-rays through a crystal plate and observed the reflexion from the interior planes. In this case the equations for the multiple reflexions take quite a different form from (7·1). Suppose the crystal cut into layers parallel to its faces, the breadth of a layer being δx. Let $I_u(x)$ be the power of the incident beam at depth x from the front face, $E_u(x)$ of the reflected beam. Let B be the area of the face on which the rays fall. The incident beam now makes angle $\theta+u$ with the *normal* to B, and so the intensity is $I_u(x)/B\cos(\theta+u)$. The power reflected in the volume $B\,\delta x$ is $I_u(x)\,\delta x\,G(u)\sec(\theta+u)$ and the incident ray is reduced by an amount

$$I_u(x)\,\delta x\,\{\mu+G(u)\}\sec(\theta+u).$$

Similarly for the reflected rays. The differential equations now are

$$\left.\begin{aligned}\frac{\partial I_u(x)}{\partial x}&=-\frac{\mu+G(u)}{\cos(\theta+u)}I_u(x)+\frac{G(u)}{\cos(\theta-u)}E_u(x)\\ \frac{\partial E_u(x)}{\partial x}&=-\frac{\mu+G(u)}{\cos(\theta-u)}E_u(x)+\frac{G(u)}{\cos(\theta+u)}I_u(x)\end{aligned}\right\}. \quad (8{\cdot}1)$$

The end condition is that $E_u(x)=0$ for $x=0$. If E_u is the power of the emerging reflected beam, the solution gives

$$E_u/I=\frac{G(u)}{\cos(\theta+u)}\,\frac{\sinh\tau x}{\tau}\exp-\frac{x\{\mu+G(u)\}\cos\theta\cos u}{\cos(\theta+u)\cos(\theta-u)}, \quad . \; . \; . \; (8{\cdot}2)$$

where

$$\tau=\frac{\sqrt{G^2\cos(\theta+u)\cos(\theta-u)+(\mu+G)^2\sin^2\theta\sin^2u}}{\cos(\theta+u)\cos(\theta-u)}.$$

Apart from the first factor in (8·2), u only occurs as a square. So, as in § 7, an averaging with the reversed beam will eliminate the effect of untrue faces. In most cases this will be far less important than it was in § 7, because the factor occurs as a cosine and in the important cases θ will be fairly small.

The exponential and hyperbolic functions can always be expanded, and if $G(u)/\mu$ is not large the series will converge rapidly. It will usually be right to omit the terms involving $\sin^2 u$, etc., even though some of these are multiplied by μ and are being compared with others only multiplied by $G(u)$. Then

$$\tau = G(u) \sec\theta$$

and

$$E_u/I = e^{-\mu x'}[x'G(u) - x'^2G^2(u) + \tfrac{2}{3}x'^3G^3(u)], \quad . \quad (8\cdot3)$$

where x' is written for $x \sec\theta$. As in § 7, if the form of E_u/I is found experimentally, it is possible to solve (8·3) and so to obtain $G(u)$, and consequently Q', from observation of a single crystal. In this case the process will be free from the objection raised in § 7 about non-uniform distribution of the blocks; for, in reflecting, the surface does not now receive preferential treatment over the interior. The primary extinction is again untouched by the process.

Bragg adopted a method which assumed that he could get a series of plates of various thicknesses, for all of which the distribution of the blocks was the same. He took the integrated reflexion of them, and found for each set of reflecting planes the thickness which gave maximum reflexion and the height of the maximum. Now by (7·4) the integrated reflexion may be written as

$$\rho = \int_{-\infty}^{\infty} (E_u/I)\, du = e^{-\mu x'}[Q'x' - g_2 Q'^2 x'^2 + \tfrac{2}{3} g_3 Q'^3 x'^3]. \quad (8\cdot4)$$

This has maximum at

$$x' = \frac{1}{\mu} - g_2 \frac{Q'}{\mu^2} + \tfrac{4}{3} g_3 \frac{Q'^2}{\mu^3}, \quad . \quad . \quad . \quad . \quad . \quad (8\cdot5)$$

and the value there is

$$\frac{Q'}{\mu e}\left[1 - g_2\frac{Q'}{\mu} + (\tfrac{1}{2}g_2^2 + \tfrac{2}{3}g_3)\frac{Q'^2}{\mu^2}\right] \quad . \quad . \quad . \quad (8\cdot6)$$

$$= Q'/e\left\{\mu + g_2 Q' + (\tfrac{1}{2}g_2^2 - \tfrac{2}{3}g_3)\frac{Q'^2}{\mu}\right\}. \quad (8\cdot7)$$

Thus Bragg's work determines g_2Q', and if the distribution of the blocks is the same as in the crystal used for the work of § 7, it follows that his correction for secondary extinction is correct to the second order, and from the magnitudes of the quantities involved it is improbable that the third order is sensible.

9. *Comparison with Experiment.*

There is not a great deal of material suitable for testing these formulæ, and the result of the test is not very satisfactory. The first point of comparison is the curve in B.J.B. ii. p. 12, which relates the modified absorption coefficient to the integrated reflexion of a face. The ordinate of the curve is given by (8·7) and its abscissa by (7·5). The linear form of the curve means that

$$\left\{ g_2+(\tfrac{1}{2}g_2{}^2-\tfrac{2}{3}g_3)\frac{Q'}{\mu} \right\} . 2(\mu+g_2Q') \quad . \quad . \quad (9{\cdot}1)$$

is practically constant, and this it will be, if $g_2{}^2Q'$, g_3Q' are negligible compared with $g_2\mu$. Neglecting these terms we find

$$2g_2\mu=5{\cdot}6\div(5{\cdot}41\times10^{-4}),$$

whence $g_2=484$. This may be best interpreted by assuming an error law of distribution as in (5·7). Then

$$G(u)=Q'e^{-u^2/2\sigma^2}/\sqrt{2\pi}\sigma \quad \text{and} \quad g_2=\sqrt{\pi}/2\sigma,$$

which gives $\sigma=6'$. This is a good deal smaller than would be expected from the general description of the experiments; for it means that all the reflexion should take place within less than half a degree, whereas the paper implies that the band of reflexion was nearly a degree broad. A part of the discrepancy may be due to the neglect of the further terms in (9·1), for it is evident that the series is not very rapidly convergent, when, as here, $g_2Q'/\mu=5{\cdot}6/10{\cdot}7$.

A more detailed, but still less satisfactory, comparison may be made with the reflexion curves of B.J.B. ii. p. 13. The experiments dealt with the reflexion through two plates of the same thickness, of which the surfaces had been differently treated. The information about the curves is not quite complete, but can be supplied indirectly. It is first necessary to find the absolute values of E_u/I. The curves are drawn in arbitrary units, and a constant multiplier must be obtained for each from the observed value of its integrated reflexion (which is the area of the curve), in terms of that of a standard plate of the same thickness. The reflexion of the standard was calculated (p. 7) from that of a face, on the principle that for a surface the integrated reflexion is $Q'/2(\mu+g_2Q')$, while for a plate of thickness giving maximum reflexion it is $Q'/e(\mu+g_2Q')$. There is thus the assumption that the plate has the same scatter as the face.

However, from these data it is possible to get the numerical values of E_u/I for all values of u. It is found that the approximation of (8·3) is quite accurate enough, and this equation can be solved for $G(u)$. A quadrature then gives Q'. The results are rather disappointing, for the curve A gives $Q' = {\cdot}0119$, while B gives $Q' = {\cdot}0146$. Moreover, the extinction coefficients g_2Q' come out as 1·01 and 0·47 respectively, whereas values in the neighbourhood of 5 would have been expected. The discrepancy is exactly the same as in the evaluation of g_2 above. There it was found that the region of reflexion ought to be narrower for the observed extinction, here that the observed reflexion curve implies less extinction than is in fact found. It is, of course, possible that a part of the difference between A and B may be due to a difference of their primary extinctions, and the cause suggested at the end of § 7 may be another source of discrepancy.

Finally, our results may be applied to some experiments due to Davis and Stempel *. Here the perfection of the calcite crystal was enormously greater than in Bragg's rock-salt, and all the approximations are hopelessly wrong. If, nevertheless, we apply our formulæ to the actual curves we may obtain something of an idea of the perfection of the crystal. The data are directly in terms of E_u/I. They were dealing with white X-rays, but there was double reflexion in two crystals with parallel faces and it is easy to see that dispersion will play no part, so that the formulæ for monochromatic rays are applicable. Taking the most extreme case of all, their fig. 6 (p. 617), we use (7·6) to obtain $G(u)$ and from this we get a scatter $\sigma = 4''{\cdot}8$. Now this is only a little greater than what should be the region of complete reflexion in a perfect crystal, and the most remarkable thing about it is that not more than half the incident beam is reflected. This suggests that a part of the breadth of the reflexion is really due to imperfection. It does not appear worth while to carry further the comparison with these experiments, both because our methods are not applicable rigorously, and because there must certainly be a great deal of primary extinction in crystals that are so nearly perfect, so that they would be of little use in a determination of Q.

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* Davis and Stempel, Phys. Rev. vol. xvii. p. 608 (1921).

10. *The Powder Method.*

From the preceding sections it appears that the phenomenon of primary extinction is likely to make serious difficulty in determining Q by the method of reflexion, whether from a face or through a plate. The only way to ensure its absence is to use crystals so small that it is bound to be negligible. For example, from the numerical data of § 6, primary extinction would be absent, if the crystals were so small as to be just about invisible under a high-power microscope. The only practicable way of using such is by the powder method of Debye and Hull, which has recently been used quantitatively by Sir W. H. Bragg [*]. For the sake of completeness we shall apply our processes to this, adopting an arrangement which is probably not the most convenient, but which could easily be modified.

We shall suppose a speck of powder is illuminated by rays and shall find the total power thrown off into a cone (of half-angle 2θ), corresponding to one particular set of planes. Let the volume be V and let it be composed of small blocks, the typical block being of volume W with normal in the direction of colatitude and longitude ω, ϕ. Let the distribution of the blocks be given by

$$\mathrm{VF(W)}\,d\mathrm{W}\sin\omega\,d\omega\,d\phi. \quad . \quad . \quad . \quad (10{\cdot}1)$$

F is nearly the same as in § 5, but is now independent of ω, ϕ, as they are pointed equally in all directions. We have then

$$4\pi\int \mathrm{W\,F(W)}\,d\mathrm{W}=1,$$

ω is the inclination of the normal to the incident beam, and so $\omega=\frac{\pi}{2}-\theta-u$. Multiplying (4·5) by the appropriate factors we have for the whole reflected power arising from this set of planes

$$\mathrm{JN}^2 f^2\cos^2\theta\,.\,\mathrm{V}\int^{(3)}\mathrm{F(W)}\,d\mathrm{W}\,du\,d\phi\int^{(2)}dv\,d\psi\int_{\mathrm{W}}^{(6)}d\mathrm{V}\,d\mathrm{V}'$$
$$\exp ik\,\{(x-x')(u-v)\sin\theta+(y-y')\psi\cos\theta$$
$$-(z-z')(u+v)\cos\theta\}. \quad . \quad (10{\cdot}3)$$

Here J is the incident intensity and of the factor $\cos^2\theta$ one term is due to the $\sin\omega$, the other to the $r^2\cos\theta\,dv\,d\psi$ integration. The integrations follow the same course as

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[*] W. H. Bragg, Proc. Lond. Phys. Soc. vol. xxxiii. p. 222 (1921).

those in § 4. The result is *

$$\tfrac{1}{2}\mathrm{JV}\cos\theta\,.\,\mathrm{Q}. \quad . \quad . \quad . \quad . \quad . \qquad (10{\cdot}4)$$

This must then be multiplied by a numerical factor given by the symmetry of the crystal according to the following rule. If the crystal has no centre of symmetry, add one on to its symmetry elements. Now construct the "form" corresponding to the planes that are being studied. The number of its faces is the required numerical factor for (10·4) ; by virtue of the centre of symmetry it must always be an even number. For example, in rock-salt the form for (1, 0, 0) is a cube and the factor is 6 ; for (1, 1, 0) it is a rhombic dodecahedron and the factor is 12 ; for most planes the number is 48. It may sometimes be necessary to apply a correction for absorption. This will depend on the shape of the powder and is a matter of simple geometry. It should not be necessary to make any allowance for secondary extinction, but if it were needed it could be calculated on the principles of §§ 7, 8.

11. *Discussion of Results.*

The tests in § 9 were rather unsuccessful, but I do not think sufficiently so to condemn our theory out of hand. Should further tests prove that the discrepancy is real, it appears to me that it would throw doubt, not only on my own work, but also on the validity of the deduction of Q in B.J.B. ii. ; for that deduction can only be founded on some theory which must be the same as the present one in principle.

It is of course possible that a crystal, imperfect by warping instead of cracking, should obey a different rule, but I should judge this to be very unlikely. For (5·5) may be used to define a function G(*u*) for such a crystal, though its expression in terms of the imperfection will not be so easy as for a cracked crystal. With this G(*u*), the work of §§ 7, 8 will all stand good, and will determine the relation between the extinction and the breadth of the reflexion region, without touching the question of the meaning of G(*u*). As to this last, it is a most natural conjecture that (5·6) will be true for it, in view of the generality which that equation has already been proved to possess, and so will lead to the right value for Q. If, as appears probable, rock-salt is warped rather than cracked, this will have the advantage that primary extinction is unlikely to be important, and so the

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* The expression does not vanish for $\theta=\pi/2$ on account of the factor cosec 2θ in Q.

interpretation of experiments will be freed from a source of error, the amount of which must be very uncertain.

We therefore conclude that, to establish beyond doubt the validity of the work of Bragg, James, and Bosanquet, it is essential that the work of §§ 7, 8 should be verified by tests like those of § 9, and if it should be proved correct, then we may have great confidence in their results. Failing this verification, the theory on which they eliminated the extinction is without good foundation and the results must be regarded with some caution. In this case, it seems to me that the most satisfactory way of determining Q is by the powder method of § 10.

Summary.

The paper is a theoretical inquiry into the possibility of determining the arrangement of electrons in the atom from the intensities of the X-rays scattered by crystals. This problem falls into two stages: first from crystal to molecule, then from molecule to electrons—only the first stage is here treated.

Simple formulæ have been given by various writers, and the process has been carried out experimentally by Bragg, James and Bosanquet. They encountered the difficulty of "extinction." This extra absorption falsifies the formulæ, but they measured it directly and so obtained a correction. This paper is concerned with seeing whether their correction was valid. The point of the problem was known to lie in the imperfection of crystals.

After a general discussion (§§ 1, 2, 3), it is shown (§ 4) that if a small perfect crystal of any shape is turned through the reflecting angle for monochromatic rays, the amount of reflexion determines a quantity Q, which is what is required for the second stage of the problem.

The reflexion is worked out (§ 5) for a conglomerate of small blocks of perfect crystal all orientated nearly in the same direction, the conglomerate being so thin that absorption and extinction can be neglected.

Extinction—that is, the special absorption of rays at the reflecting angle—is shown (§ 6) to lead to two effects, primary and secondary. The primary diminishes the reflexion from a perfect crystal below the amount given by the simpler theory. It leads to a change in the value of Q depending on the depth of the crystal, and none of the experimental processes eliminate this change. The secondary extinction results from the reduction in the strength of the beam transmitted through the crystal.

The reflexion from the face of a deep imperfect crystal is evaluated (§ 7), and it is shown how the secondary extinction may be eliminated.

The same process for reflexion from the interior planes of a plate is worked out (§ 8), and the formulæ are justified whereby Bragg, James, and Bosanquet eliminated the extinction—but only the secondary extinction.

The theoretical results are compared with experiment (§ 9). The experimental data are rather inadequate and the agreement is not very good.

The corresponding calculations are done for the powder method of observation on crystals (§ 10).

The paper concludes with a short discussion (§ 11), suggesting the need of further tests.

XCIII. *Scattering and Dispersion of Light.* By U. Doi, *Research Student in the Institute of Physical and Chemical Research, Tokyo* [*].

AUTHORS differ in their opinions as to the mechanism of scattering light by a medium through which the light travels. Schuster asserts, however, in his 'Theory of Light' (p. 325) that, if a molecule of the medium may be looked upon as a separate source of scattering, the scattering due to it follows undeviatedly the celebrated formula of Lord Rayleigh, whatever be the theory we adopt. It will not be without interest, for instance, to notice that Jakob Kunz [†], indeed, derived exactly the same formula from an elementary theory of scattering of light by small dielectric spheres.

Ever since the electron theory of matter began its striding progress, and the well-known dispersion formula was deduced by H. A. Lorentz through his electronian analysis of atomic constructions, attempts have been made to interpret the absorption of light from the electronian standpoint of view. Thus, Drude [‡] and Voigt [§] attribute it to the damping of the oscillations of bound electrons in the atoms of the absorbing medium, the damping process being caused by a resisting force proportional to the velocity of the electrons. They insert consequently a term of this damping in the equation of motion of

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[*] Communicated by the Author.

[†] Phil. Mag. xxxix. p. 416 (1920).

[‡] P. Drude, *Lehrbuch der Optik*, p. 353.

[§] W. Voigt, *Magneto- und Electrooptik*, p. 104.

an electron. Lorentz[*] assumes on the contrary that there is no damping, but that the electron can continue to vibrate further and further, restrained only by radiation, until the molecule collides with another. When this happens, he assumes that all the energy of the vibration will be transferred to energy of translation, or thermal agitation as it is called, of molecules. The effect of this he proves equivalent to a damping force $-\frac{2m}{\tau}\frac{dr}{dt}$, where m is the mass of an electron, and τ is the mean time between collisions of molecules. Thus, defining the absorption coefficient k by the equation

$$\frac{d\mathrm{I}}{dx}=-k\mathrm{I},$$

he finds[†]

$$k=\frac{4\pi n^2 g\mathrm{N}e^2/c}{m^2({n_0}'^2--n^2)+n^2g^2}, \quad \left(g=\frac{2m}{\tau}\right).$$

The meanings of the notations may need no explanation, as one is, if necessary, rather preferably referred to the original.

It seemed, next, to Nagaoka[‡] and Planck[§] that the reaction, $\frac{e^2}{6c^3}\dddot{\xi}$, to the radiation of an electron, when it has an acceleration, $\ddot{\xi}$, will act frictionally. Along this line of idea Planck derives the coefficient of extinction, which agrees with Rayleigh's formula for the scattering coefficient. The general process of deriving the coefficient is to insert a term of this frictional force in the equation of motion of the electron, and to calculate the energy dissipated in overcoming this friction. The calculation, however, requires too complicated a process to be summarized here clearly.

Be that as it may, the scattering is another thing, in a rigorous sense, than the extinction or absorption; and the calculation of what part of the energy of the incident radiation is dissipated in overcoming any frictional force exerted by molecules of the medium through which the light travels, does not offer us any means of deducing the coefficient of scattering, as the energy absorbed by the medium is not all scattered by it,—a part, at least, of the absorbed energy is converted, as we know, to the heating agent of the medium,

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[*] H. A. Lorentz, 'The Theory of Electrons,' p. 141 (1916).

[†] Phys. Rev. iv. p. 189 (1914).

[‡] Proc. Tokyo Math.-Phys. Soc. ii. p. 280 (1904).

[§] *Sitzungsber. d. Kgl.-Pr. Akad. d. Wiss.* p. 748 (1904).

though for a gaseous medium it is general to disregard the heating effect accompanying the absorption, and consequently to make no marked distinction between the scattering and the absorption or extinction.

In order to deduce more rationally the coefficient of scattering, therefore, we have to resort to another process of calculation; an answer to this request will be obtained through identifying the scattered energy with the energy of radiation itself from the electron which is set in motion forced by the incident light. The amount of radiated energy, then, must be measured by $\frac{e^2}{6\pi c^3}\ddot{\xi}^2$ *, where e is the charge of the electron, and c the light velocity in vacuum, while $\ddot{\xi}$ is the acceleration of the vibratory motion of the electron. It will be noticed here that no term needs to be added to the equation of motion of the electron corresponding to a reaction to the radiation from it, as it is too small to affect the general features of the problem when we attack it from this side. Let us take, then, the Lorentz equation of motion of an electron for the case of a plane polarized wave incident on it, in which no term of damping appears, namely, of the form †

$$m\frac{d^2\xi}{dt^2}=e(\mathrm{E}_x+a\mathrm{P}_x)-f\xi,$$

where ξ is the displacement of the electron from its position of equilibrium, a a constant nearly equal to $\frac{1}{3}$ (Heaviside-Lorentz Units of electromagnetism are adopted here), f another certain positive constant that characterizes the elastic force of restitution of the electron, and P_x, the polarization within the medium caused by the electric vector E_x of the incident light.

Denoting by N the number of polarized particles per unit volume of the medium,

$$\mathrm{P}_x=\mathrm{N}e\xi \ddagger.$$

Thus
$$m\frac{d^2\xi}{dt^2}=e(\mathrm{E}_x+a\mathrm{N}e\xi)-f\xi,$$

or
$$m\frac{d^2\xi}{dt^2}+(f-a\mathrm{N}e^2)\xi=e\mathrm{E}_x.$$

Supposing the light vector to be a periodic function of the frequency n, say $\mathrm{E}_x=\mathrm{X}_0\epsilon^{int}$ at a point, and putting the frequency of the free vibration of the electron, as usual,

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* O. W. Richardson, 'The Electron Theory of Matter,' p. 256.

† H. A. Lorentz, 'The Theory of Electrons,' p. 309.

‡ *Ibid.*, p. 136.

$\sqrt{\frac{f}{m}}=n_0$, we obtain, for the general solution of the above differential equation

$$\xi=\frac{e}{m}\frac{X_0\epsilon^{int}}{n_0^2-n^2-aNe^2/m}+A\epsilon^{in_0t}+B\epsilon^{-in_0t},$$

in which A and B are arbitrary constants of integration.

We have to observe at this point of discussion that there is every reason to suppose that within a medium the radiation and absorption due to *free* vibrations of the electrons compensate each other, so that in consideration of the present problem of scattering of light incident on them from an external system, we may naturally put the terms of *free* vibrations out of consideration, limiting our attention solely to the part of *forced* vibration,

$$\xi=\frac{e}{m}\frac{X_0\epsilon^{int}}{n_0^2-n^2-aNe^2/m}.$$

Differentiating ξ twice as to time,

$$\ddot{\xi}=-\frac{e}{m}\frac{n^2X_0\epsilon^{int}}{n_0^2-n^2-aNe^2/m}$$

The amount of radiation corresponding to this acceleration is

$$\frac{e^2}{6\pi c^3}\ddot{\xi}^2=\frac{e^2}{6\pi c^3}\left(-\frac{e}{m}\frac{n^2X_0\epsilon^{int}}{n_0^2-n^2-aNe^2/m}\right)^2$$

$$=\frac{e^4n^4X_0^2\epsilon^{2int}}{6\pi c^3m^2(n_0^2-n^2-aNe^2/m)^2}.$$

This energy of radiation must be consumed from the incident energy, which results in scattering after all. Take, now, a thin lamina of the medium, of a thickness dx and cross-section A, perpendicular to the incident ray of light. The number of scattering electrons contained within this elementary lamina will be NA . dx, so that the amount of energy radiated from this lamina during a time-interval t is

$$NA\,.\,dx\int_0^t\frac{e^2}{6\pi c^3}\ddot{\xi}^2dt$$

$$=NA\,.\,dx\frac{e^4n^4X_0^2}{6\pi c^3m^2(n_0^2-n^2-aNe^2/m)^2}\int_0^t\epsilon^{2int}dt.$$

But the energy incident on this lamina during the same interval of time is*

$$I=A\,.\,c\,.\int_0^t X_0^2\epsilon^{2int}dt$$

$$=A\,.\,cX_0^2\int_0^t\epsilon^{2int}dt.$$

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* *Cf.* O. W. Richardson, *loc. cit.* p. 211.

Thus, the scattered energy is

$$-d\mathrm{I}=\mathrm{NA}\,.\,dx\,\frac{e^4n^4\mathrm{X}_0{}^2}{6\pi c^3m^2(n_0{}^2-n^2-a\mathrm{N}e^2/m)^2}\int_0^t \epsilon^{2int}dt$$

$$=\frac{\mathrm{N}dxe^4n^4}{6\pi c^4m^2(n_0{}^2-n^2-a\mathrm{N}e^2/m)^2}\,.\,\mathrm{I}.$$

Then, defining the coefficient of scattering κ by the equation

$$d\mathrm{I}=-\kappa\mathrm{I}dx,$$

we have

$$\kappa=\frac{\mathrm{N}e^4n^4}{6\pi c^4m^2(n_0{}^2-n^2-a\mathrm{N}e^2/m)^2}.$$

Again, if we denote by μ the refractive index of the medium, we have *

$$\mu^2-1=\frac{\mathrm{N}e^2}{m}\,\frac{1}{n_0{}^2-n^2-a\mathrm{N}e^2/m}.$$

Hence
$$\kappa=\frac{n^4}{6\pi c^4\mathrm{N}}(\mu^2-1)^2.$$

Putting
$$n=\frac{2\pi c}{\lambda},$$

$$\kappa=\frac{16\pi^3}{6\mathrm{N}\lambda^4}(\mu^2-1)^2$$

$$=\frac{8\pi^3}{3}\,\frac{(\mu^2-1)^2}{\mathrm{N}\lambda^4}.$$

If we put further

$$\mu^2-1\doteqdot 2(\mu-1),$$

we have finally

$$\kappa=\frac{32\pi^3}{3\mathrm{N}}\,\frac{(\mu-1)^2}{\lambda^4},$$

which is Rayleigh's formula for the scattering coefficient for a gaseous medium †.

The correctness of this formula is acknowledged generally. and its experimental verifications, too, are not wanting, the latest and most extended treatment of the subject being given by Cabannes in *Annales de Physique*, vol. xv. Jan.–Feb. 1921. (There will also be found in it a complete list of authors and works in this direction.)

As for the theoretical deduction of the formula, the suggestion is given in Lorentz's 'Theory of Electrons' (p. 309, Note 56*), and Natanson ‡ also derives the form after a long and more or less complicated discussion. But so far as I am aware, the way above indicated seems the simplest one to arrive at the result.

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* H. A. Lorentz, *loc. cit.* p. 144.

† Phil. Mag. [5] xlvii. p. 379 (1899).

‡ Phil. Mag. xxxviii. p. 269 (1919).

It will hardly be necessary to remark that, along this line of argument, when the frequency of the incident wave is very near to that of proper oscillation of the electrons in atoms, there takes place a resonance phenomenon, and as the result of this there may be expected to occur such phenomena as ionization and resonance radiation of the gas, and the incident energy thus being consumed by a considerable amount, the spectrum line corresponding to this frequency will be missing, which is called an absorption line in the ordinary spectroscopy.

Physical Institute, College of Science,
Imperial University of Tokyo,
Sept. 20, 1921.

XCIV. *Observations and Experiments on the Occurrence of Spark Lines (Enhanced Lines) in the Arc.*—Part II. *Magnesium, Zinc, and Cadmium.* *By* G. A. HEMSALECH *and* A. DE GRAMONT *.

[Plates XVII.–XXI.]

CONTENTS.

§ 1. *Introduction.*

AS a result of an experimental investigation of the arc spectra of lead and tin described in an earlier communication † we arrived at the conclusion that the emission of spark lines (enhanced lines of the fourth type of Hemsalech's classification) by the arc is connected with the presence of strong electric fields. Further, we showed that when the temperature of the medium is raised, by

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* Communicated by the Authors.

† G. A. Hemsalech and A. de Gramont, Phil. Mag. ser. 6, vol. xliii. p. 287 (1922).

means of a white-hot carbon cathode, the spark lines disappear from the spectrum of the metal vapour. Thus the prominence of spark lines in the spectrum of a source appeared to indicate that the temperature of the latter must be relatively low. In fact the spark lines of lead were found to be strongly emitted by an arc burning under liquid air—namely, at a temperature of about −190° C. Encouraged by these results, we first made a general survey of the arc spectra of fifteen different metals by means of the methods previously described, and then devoted our attention more particularly to the spectrum of magnesium. This element was marked out for special examination not only by reason of its cosmical importance but also because its spectrum contains four distinct types of radiations, all of which occupy in turn prominent positions in the various laboratory sources of light. It therefore seemed to us that a detailed study of the spectrum of magnesium might lead to results of a more general interest on account of the possibility of investigating in one and the same spectrum the relative behaviour of four different types of radiations under the special conditions prevailing in our experiments. It may be useful for the better understanding of what follows to briefly recall our present knowledge concerning the emission of these four types of magnesium lines comprised within that region of the spectrum which is of particular interest to the astrophysicist, namely from λ 3600 to λ 7000 :—

First type.	Flame line λ 4571. Observed already at the temperature of the air-coal gas flame.
Second type.	Series triplets at λ 3838 and λ 5184. These lines are absent from the mantle of the air-coal gas flame. λ 5184 has been observed in the oxy-hydrogen flame. Both triplets are emitted by the flame of burning magnesium. Their emission is very strong under thermo-electrical excitation in the fringe of a single plate resistance furnace. They are likewise brought out under chemical excitation in the blue cone of the air-coal gas flame. Strong in arc and spark.
Third type.	Rydberg's nebulous series, of which the least refrangible line in this region is λ 5528. With certainty observed only in arc and spark.
Fourth type.	Spark lines of which the most prominent and important is λ 4481. Not seen in any of the flames nor in the furnace. Traces only in ordinary arc in air between Mg poles. Brought out strongly in arc under water or in hydrogen. Very intense in capacity spark.

The second and third type lines constitute the so-called arc lines.

In addition to a detailed account of our experiments with magnesium the present communication contains also the results of our observations on the enhanced lines of the related elements zinc and cadmium.

The methods of producing and of observing the various kinds of arcs were the same as those described in our first communication.

§ 2. *Influence of the nature of the liquid film upon the emission of various types of lines in the arc.*

In an arc flash passing between magnesium poles through a liquid film the first phase is generally sharply defined, and the character of the spectrum changes almost abruptly on passing from the first to the second phase. The relative behaviour of the various types of magnesium lines is probably controlled by the conditions which predominate at the various stages of development of an arc flash. Thus, if certain chemical reactions took place between the magnesium vapour evolved and the liquid or one of its constituents, such an event might reveal itself by some special peculiarity of the spectrum and the latter would change on passing from a liquid of one kind to one of a different chemical constitution. Again, if any particular group of lines were influenced by the electric field set up within the first phase, the effect should be the same for all liquids whatever may be their composition. Of the three liquid films used with magnesium—namely, water, glycerin, and paraffin oil, the first two contain oxygen, and we might therefore expect to observe effects of possible oxidation. Indeed we find that whereas in the water and glycerin films the flame line 4571 is well developed, only faint traces of it are seen in the paraffin-oil film. In like manner the well-known band at λ 5007, which is generally ascribed to the formation of an oxide, is brought out in the water and glycerin films but is absent from the paraffin-oil film. In the second phase or the arcing stage the flame line as well as the bands are brought out in all three cases. During this phase the arc flash is of course exposed to the influence of the surrounding air containing oxygen. Thus, it would seem that the emission of the flame line λ 4571 under these conditions is favoured, though not solely controlled, by the presence of oxygen.

The lines of the second type, namely the triplet series, on the other hand, are not affected by the nature of the film.

They are strongly emitted throughout the arc flash, though slightly enhanced and symmetrically widened in the first phase; hence these lines appear to be sensitive to the intense electric actions of which the liquid film is the seat. This observation is therefore quite in keeping with the known behaviour of the triplets in the single plate resistance furnace.

The lines of the Rydberg series, which form the third type, are hardly visible in the layer of paraffin oil though very intense in the water and glycerin films. A special character of these lines is their tendency to expand towards the red. The wings thus formed are particularly well developed in the water film; but they also remain a prominent feature during part of the second phase of both the water and glycerin arcs, and, what must be considered a significant event, they disappear abruptly, the emission continuing as narrow symmetrical lines till the cessation of the luminous phenomenon. In the paraffin-oil arc the third type lines attain their maximum of development only towards the end of the second phase. From these few results it is, however, difficult to derive any definite conclusions as to their origin or mode of excitation under these particular conditions, and, although we feel inclined to assign their emission in the main to electric forces, their great feebleness in the paraffin-oil film seems to point to the necessity of concurrent chemical actions.

With regard to the spark lines, these form a most prominent feature of the spectrum emitted during the film stage with all three liquids. In particular the line λ4481 shows an extraordinary development and, as regards relative intensity and width, approaches its characteristic appearance in a capacity spark. The symmetrical broadening of this line is greatest in the water film. During the second phase its breadth diminishes very rapidly and, at a definite moment, its intensity falls off quite abruptly, the line continuing as a narrow and feeble one. The abrupt drop in intensity of this line, both in the water and glycerin arcs, occurs at the same instant as the sudden disappearance of the red wings of the third type lines, as though the radiating centres were at this moment undergoing some profound modification in their constitution.

The three liquids employed—namely, distilled water, paraffin-oil, and glycerin, are bad conductors of electricity, and it might therefore be contended that films of these liquids placed between the poles act as dielectrics. That this is, however, not the case was shown by placing a drop of a concentrated solution of magnesium sulphate between poles of magnesium metal. The effect of the well-conducting film upon the various types of lines was found to be the same as that of the non-conducting water film. Experiments were also made with the object of ascertaining whether the spark lines could be excited in the liquid medium itself without the projection of metal vapour from the electrodes. A drop of magnesium sulphate solution was placed between graphite poles, and the arc flash produced in the usual way. The general character of the spectrum thus obtained was found to be similar to that observed when the arc passes between electrodes of magnesium metal through a water film. Thus, for example, in the first phase the spark line λ 4481 is symmetrically widened and the lines of the Rydberg series are winged on the red side.

The effect of liquid films of various composition has likewise been investigated in the case of zinc and cadmium. The relative behaviour of the spark and arc lines of these elements during the first and second phases is very similar to that shown by the corresponding lines of magnesium. It may be mentioned in this connexion that a film of alcohol proved equally successful in bringing out the spark lines of cadmium. It thus appears from the whole of our observations that the emission of spark lines in the arc is independent of the nature of the liquid placed between the electrodes.

§ 3. *Effect of high voltage currents.*

In all the experiments described in the preceding paragraph the electric current used for producing the arc was supplied at 80 volts. In a subsequent series of experiments the arc was fed from a 200 volts circuit. The most striking effect of the higher voltage in the case of the water arc between magnesium poles is the remarkable development of the whole second phase emission. This is probably due to the rather intense arc flash which follows the destruction of the liquid film.

The lines most particularly affected by the higher voltage are those of the Rydberg series and λ 4481. During the first phase and the early stages of the second the former are strongly winged and hazy, but during the greater part of the second phase they appear as bright and well-defined though not absolutely sharp lines. The lines of the triplet series are symmetrically widened in the film and at the beginning of the arc flash, but afterwards they are narrow and well defined as in an ordinary arc. A most noteworthy behaviour characterizes the spark line λ 4481. During the first phase it shows the usual symmetrical expansion, but in the second phase it appears as a fairly sharp bright line which at a certain definite moment stops quite abruptly whilst all the other lines continue and are not even affected in their intensities. This curious fact clearly indicates that some factor absolutely essential to the emission of λ 4481 either disappears suddenly at this moment or reaches some critical minimum value below which it is no longer capable of stimulating this particular radiation.

High voltage experiments have likewise been made with concentrated solutions of magnesium sulphate and chloride between graphite poles. In the case of the sulphate solution the lines of the Rydberg series are the most affected; they are winged on the red side during the first phase and in the early stages of the arc flash. The flame line λ 4571 is absent, as it also is with the 80 volts arc; but the band at λ 5007 shows throughout the arc flash. The triplets and the spark line λ 4481 are enhanced as compared with the low voltage spectrum. With a chloride film, under otherwise similar conditions, the magnesium spectrum appears on the whole more feebly developed. Nearly all the lines in the first phase are intensified or widened as compared with their appearance during the subsequent arc flash. The flame line λ 4571 and the band at λ 5007 are absent; the lines of the Rydberg series show only as traces in the film spectrum. The series triplets and the line λ 4481 rise to the same level in the second phase, thus indicating that also in this case λ 4481 is particularly affected by the more powerful arc flash. A similar effect of the higher voltage upon spark lines has been noted in the case of cadmium by using a film of a concentrated solution of the chloride of this element between poles of graphite, namely the two spark lines λ 5338 and λ 5379 attain almost the same level as the arc lines.

As a general result of our observations on high voltage arcs, we are led to conclude that the application of a high potential appreciably prolongs the life of the spark lines during the second phase and, when the arc passes between poles of magnesium metal, brings into prominence the lines of the Rydberg series.

§ 4. *Thickness of liquid film at moment of rupture, and relative durations of the first and second phases.*

As was explained in § 5 of our first communication, the introduction of a liquid film between the poles of an arc gives rise to a transient luminous phenomenon composed of two distinct phases, the durations of which are largely controlled by the speed of the upward-moving electrode and by the thickness of the liquid film at the moment of its rupture. Further, during the course of development of this arc phenomenon certain spectrum lines stop or diminish in intensity quite abruptly at the end of the first phase, others suddenly cease to be emitted at some definite point during the second phase, whilst some again continue till the end of the luminous flash. It seemed to us that a more precise knowledge of the exact positions of the various levels up to which particular radiations are emitted might possibly be of help in revealing the nature of those factors which govern the production and development of the liquid film arc. Accordingly measurements were made of the thickness of the liquid film and of the relative altitudes of those points which mark certain abrupt changes in the emission of a few characteristic lines. The maximum duration of the luminous arc flash was considered to be given by the length of the arc lines, such as λ 5184 of magnesium. These measurements were made on the spectrograms and reduced to actual value by allowing for the magnification of the spectrum image, which in our case was equal to 1·2 times for the green and blue regions of the spectrum. The following values were obtained for magnesium with films of various liquids and solutions, assuming that the thickness of the film corresponds to the height of the spectrum in the first phase:—

	Nature of liquid film.	Thickness of liquid film.	Height from stationary electrode of	
			λ 4481.	λ 5184.
Arc at 80 volts.	Glycerin	0·12 mm.	0·95 mm.*	2·77 mm.
	Paraffin oil	0·48 ,,	1·04 ,, †	6·7 ,,
	Water..................	0·10 ,,	1·51 ,,	4·76 ,,
	Magnesium sulphate solution between Mg poles	0·20 ,,	1·67 ,,	2·30 ,,
	Magnesium sulphate solution between graphite poles ...	0·15 ,,	1·54 ,,	1·94 ,,
Arc at 200 volts.	Water	0·09 ,,	4·33 ,,	>6·6 ,,
	Magnesium chloride solution between graphite poles ...	0·08 ,,	2·40 ,,	3·09 ,,

* Continues as a narrow line throughout flash.

† After the abrupt drop in intensity at this point the emission continues as a faint narrow line up to 3·98 mm.

Thus, with the exception of the paraffin-oil arc, the thicknesses of the films are all practically of the same order of magnitude. Those obtained with the higher voltage current seem to be the thinnest: this may not merely be an accident, for it is quite conceivable that the application of a higher voltage would tend to accelerate the destruction of the film. Further, the results for the line λ 4481 show clearly that the higher voltage, while reducing the extent of the first phase, raises the critical level of the spark line. The last column gives the length of the arc flash.

Rather suggestive results were obtained for various types of cadmium lines with an 80 volts water arc, as shown by the following values :—

Thickness of film		0·09 mm.	
Heights from stationary electrode:			
Arc line..................	λ 4413 =	5·05 ,,	
3rd type enhanced line	4416 =	2·41 ,,	
Spark lines .... (first sudden drop in intensity)	5338 = 5379 =	1·26 ,, 1·23 ,,	These lines continue to be emitted faintly, and stop abruptly at a height of about 2·4 mm.

These results point to the existence of four distinct stages in the spectral development of the cadmium arc flash, namely: (1) the film stage, during which the spark lines are enhanced and symmetrically broadened; (2) a short region of the second phase marked by a strong emission of the spark lines; (3) a stage during which the spark lines are but feebly emitted and at the end of which both their emission and that of the enhanced line λ 4416 cease abruptly; and (4) the last period of the flash, during which arc lines are alone emitted. These facts seem to indicate that the emission centres, which during the first phase emit strongly all vibrations, undergo sudden changes in their constitution at several definite stages in the course of the gradual decline of the forces acting upon them. It is remarkable, although perhaps quite in keeping with the interdependance between the structure of the radiating atom and the character of the spectrum, that the abrupt stoppage of the faint portions of the spark lines λ 5338 and λ 5379 should coincide almost exactly with the equally sudden cessation of the enhanced line λ 4416.

The determination of the duration of the various phases connected with the liquid film arc requires a knowledge of the velocity with which the upper electrode moves away from the stationary one. We have made no accurate measurement of this quantity, but a rough estimate of the upward motion continued over a long range has shown us that the speed of the electrode in our experiments is in the neighbourhood of one metre per second. This result allows us to evaluate the order of magnitude of the duration of the various phases in the arc flash. Thus the principal events in the course of development of the 80 volts water arc flash between magnesium poles would be as follows :—

Moment of separation of electrodes	0·0000 second.
End of first phase	0·0001 „
Abrupt drop in intensity of λ 4481	0·0015 „
End of arc flash	0·0048 „

In a similar manner the principal epochs during the period of existence of an 80 volts water arc flash between cadmium electrodes are :—

Moment of separation of electrodes	0·00000 second
End of first phase	0·00009 „
First drop in intensity of spark lines λ 5338 and λ 5379	0·0013 „
End of emission of spark lines and of enhanced line λ 4416	0·0024 „
End of emission of arc line λ 4413, marking extinction of flash	0·0050 „

During the first phase of an arc flash the spark lines attain a development which, as regards character and relative intensity, approaches that observed in powerful condenser sparks. It is therefore of interest to compare the duration of this phase with that of an electric spark. From photographs of condenser discharges through air at atmospheric pressure taken upon a moving film by one of us, in conjunction with Sir Arthur Schuster *, we have calculated that that period of the spark which comprises the initial discharge and the rapid oscillations through the metal vapour lasts approximately 0·000016 second. It is during this short interval of time that spark lines are most strongly emitted. Now we have just seen that the time taken by the upward-moving electrode to pass through the liquid film of a water arc is about 0·0001 second, so that some of the phenomena which happened during the early stages of the progress of the electrode tip through the liquid film must have been as short-lived as the oscillating phase of a condenser spark.

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* Schuster and Hemsalech, Phil. Trans. Roy. Soc. vol. cxciii. p. 189 (1899).

§ 5. *Effects of gaseous media.*

The gases which were used in these experiments may be divided into two groups—namely, those in which a steady arc can be established between metal electrodes, such as air and nitrogen, and secondly those in which under similar electrical conditions only short arc flashes can be obtained, such as hydrogen, oxygen, and coal-gas. It seems likely that the kind of arc produced in each case is in great measure dependent upon the nature and intensity of the chemical reaction which sets in between the vaporised electrode material and the surrounding gases.

An ordinary seven-ampere arc burning steadily between magnesium electrodes in air emits the spark line λ 4481 feebly at the cathode and a little more strongly at the anode. Along the path of the arc only the merest traces of it can be detected. If, however, the observations are begun at the moment of striking the arc the spark line is seen to flash up intensely just when the electrodes separate, and it fades away again as the arc becomes established. Photographs taken of the initial stage of an arc between cadmium poles show clearly that the intensity of the spark lines falls off abruptly after the upward-moving electrode has passed through only a very small distance. In fact both the order of evolution and the general character of the spectral phenomena which mark the early stages of development of the electric arc in air are very similar to those observed with liquid films. In order to account for the strong emission of spark lines during the initial phase of an arc in air, we venture to suggest the following explanation. As the upper electrode recedes from the stationary one a more or less perfect vacuum is momentarily left between them. It is through this vacuous space or film of rarefied air that the initial stages of the discharge take place. As no air is present at first to start chemical reactions between it and the metal vapour, both conductivity and temperature of the medium remain relatively low, so that the effect of strong electric forces may develop without impediment. As soon, however, as air has penetrated the vacuous space chemical reactions set in which, by causing increase of both temperature and conductivity of the medium, lead to the establishment of a stable arc. If a current of air is blown through the arc from its commencement, ionization of the vapours is rendered more difficult and the brighter spark lines remain visible almost throughout the whole length of the arc flash during the second phase.

A remarkable effect upon the character of the spectrum of magnesium was observed with an arc burning in nitrogen. The flame line λ 4571 and the triplets at λ 3838 and λ 5184 show the usual development as given by an arc in air. The band at λ 5007 is absent, requiring probably the presence of oxygen for its emission. The Rydberg series, on the other hand, is far more developed than in air: the individual lines are much better defined and, instead of being winged towards the red, they appear only very slightly widened symmetrically. The spark line λ 4481, although relatively feeble, passes right across the space between the electrodes and appears quite sharp without any sign of haziness or broadening. Since the arc in this case was burning quite steadily, the emission of the spark line under these conditions cannot be attributed to the action of strong electric fields, for these were evidently feeble—in fact, a voltmeter indicated the existence of an average gradient of only about 150 $\frac{\text{volts}}{\text{cm.}}$. But it is possible that both the establishment of a stable arc between magnesium poles in nitrogen and the peculiarity of its spectrum are caused by some special chemical reaction between this gas and the electrode metal. As is well known, magnesium forms a nitride at high temperatures: it may therefore be that the continuous emission of λ 4481 as a narrow line and the sharpening of the lines of the Rydberg nebulous series are an optical manifestation of the process involved in the formation of magnesium nitride. In this connexion it is useful to recall the important fact observed by Dr. de Watteville that in the air-coal gas flame the series triplets of magnesium are emitted only in the explosion region [*] and, as one of us has shown, the excitation of the characteristic cone lines is most probably associated with the formation of nitrides [†]. No trace of the spark line λ 4481 or of any line of the Rydberg series has, however, been observed in the air-coal gas cone, and their emission by the nitrogen arc may possibly be brought about with the additional help of the electric current. When the observations of the arc in nitrogen are made at the instant of separation of the electrodes the character of the spectrum is similar to that of the first phase spectrum in air—namely, the lines of the Rydberg series are winged on the red side and the spark line λ 4481 is symmetrically widened. It is therefore probable that during the initial stages the light

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[*] C. de Watteville, Phil. Trans. Roy. Soc. A. vol. 204. p. 151 (1904).

[†] G. A. Hemsalech, Phil. Mag. vol. xxxiv. p. 229 (1917).

radiations both of the arc in nitrogen and of that in air are of like origin, and the explanation which we have offered for the air arc will equally well hold in the case of the nitrogen arc.

No stable arcs are formed in oxygen, hydrogen, or coal-gas under electrical conditions similar to those used in air and nitrogen—namely, with continuous current at 80 volts. The arcs consist merely of luminous flashes which show the spark lines strongly during the first phase. The prevention of a stable arc in oxygen is possibly caused by the very vigorous chemical actions which set in as soon as the arc is started. As a consequence of this the electrodes become rapidly covered with a non-conducting layer of oxide which invariably leads to the extinction of the arc. With the oxygen arc between magnesium poles the flame line λ 4571 and the bands at λ 5007 are particularly strong at the beginning of the second phase. The lines of the Rydberg series are winged on the red side, especially at the commencement of the arc flash. The spark line λ 4481 is intense and symmetrically widened in the first phase, but it remains visible as a fairly strong though narrow line throughout the flash. Whether or in how far the emission of the spark lines in the oxygen arc is caused or facilitated by the process of oxidation of the magnesium metal, our present results do not allow us to suggest. But as for the cause of emission of these lines during the first phase—namely, whilst there is paucity of oxygen in the space between the electrodes,—it is probably the same as that in the case of the air and nitrogen arcs mentioned above.

A prominent feature of the hydrogen and coal gas arcs between magnesium poles is the relatively great intensity of the spark line λ 4481. In the first phase, which also in these two arcs is probably caused by a film of rarefied gas, the line is considerably broadened out on both sides. It then suddenly falls off sharply in intensity, although still remaining strong throughout the second phase. The lines of the Rydberg series are winged on the red side and very nebulous in appearance during the whole of the arc flash. The flame line λ 4571 and the hydride bands are well developed. The series triplets present the usual normal appearance and, as was to be expected, the band at λ 5007 is absent. The hydrogen lines H_α and H_β are very intense during the first phase but much fainter during the second.

The following data have been obtained for the principal stages in the development of an arc flash between magnesium poles in hydrogen :—

Thickness of rarefied gas film		0·18 mm.
Heights from stationary electrode :	λ 4481...	1·54 „
	5184...	1·59 „
	H_{α} 6563...	0·89 „

Thus the hydrogen lines are emitted for a considerably shorter period than the metal lines. The thickness of the rarefied gas film is approximately of the same order of magnitude as that of liquid films. Measurements made on the spectrum of a blown arc in air gave 0·17 mm. as the thickness of the rarefied air film.

The following table contains a summary of the results of our observations on the appearance of the various types of magnesium lines as given by 80 volt arcs burning in various gases :—

	Air.	*Nitrogen.*	*Oxygen.*	*Hydrogen.*	*Coal-gas.*
Quality of arc......	Stable.	Stable.	Unstable.	Unstable.	Unstable.
Flame line λ 4571.	Normal.	Normal.	Normal.	Normal.	Normal.
Series triplets......	Normal.	Normal.	Normal.	Normal.	Normal.
Rydberg series ...	Diffuse.	Well-defined and prominent.	Diffuse and winged.	Diffuse and winged.	Diffuse and winged.
Spark line λ 4481 .	Diffuse, traces only.	Relatively feeble, but narrow and sharply defined.	Strong and symmetrically broadened in 1st phase; fairly strong but narrow in 2nd phase.	Very intense and symmetrically broadened in 1st phase; narrower in 2nd phase.	

§ 6. *Arc in liquid air.*

The electrodes, which consisted of metal rods, were completely immersed in the liquid, so that before the arc was struck they were at a temperature of about −190° C. With the current at 80 volts the discharge consisted in short flashes, each one of which was accompanied by the evolution of numerous air-bubbles caused no doubt by the momentary rise in temperature. Since the luminous vapour in this case is completely enclosed by liquid air its temperature cannot possibly attain a high value, and this inference is amply borne out by the relative behaviour of the flame line of magnesium λ 4571, which is only feebly excited under these conditions. In stable arcs burning between the same metal in gaseous air or nitrogen and in which the temperature reaches a high value, this line is more strongly emitted. The series triplets at λ 3838 and λ 5184 show a normal development in the liquid air arc, thus indicating that under arc conditions they are little, if at all, affected by temperature changes. The lines of the Rydberg series are well brought out and are markedly winged on the red side throughout the length of the arc flash. The spark line λ 4481 is strongly emitted, not only at the moment of striking the arc, but evenly along the whole path of the flash. Although at no stage of the liquid air arc does this line attain the remarkable breadth which characterises it in the first phase of the water or hydrogen arc, it nevertheless shows unmistakable signs of being symmetrically winged. It may also be useful to place on record the fact that the band at λ 5007 is emitted, though only faintly, in the liquid air arc.

With zinc electrodes in liquid air the arc flash obtained brings out the spark lines λ 4912 and λ 4924 strongly during the first phase; they then fall off in intensity very rapidly and only traces remain visible till the end of the second phase. The red line and the triplet in the blue, which are very intense along the whole length of the arc flash, appear strengthened and symmetrically widened in the first phase.

Our experiments with a cadmium arc under liquid air were not very successful inasmuch as we could neither observe visually nor obtain photographically any evidence of the emission of the two spark lines λ 5338 and λ 5379. It should, however, be mentioned that the whole spectrum of cadmium as obtained by us under these conditions was only feebly developed, possibly owing to the fact that poles of this metal fuse together rather readily when bringing them into contact on starting the arc. Although our observations have not brought out any interesting facts bearing on the emission of the principal spark lines of cadmium, they do, however, show up in a striking manner the difference in the behaviour of the arc line λ 4413 and the third type enhanced line λ 4416. The arc line, which is but very feebly emitted in the first phase, becomes strong as the arc flash develops during the second phase. The enhanced line, on the other hand, is strong in the first phase and changes almost abruptly into a feeble line as the second phase sets in. Thus there is here shown up a marked difference in the mode of excitation prevailing at the moment of striking the arc and during the further course of the arc flash.

In order to account for the absence of any marked differences between the first and second phase spectra of magnesium under these conditions, we venture to suggest that possibly chemical actions intervene in this case. We have already shown in § 5 that nitrogen is effective in bringing out the spark line λ 4481 and in strengthening the lines of the Rydberg series. Remembering then that the boiling-point of nitrogen (—196° C.) is lower than that of oxygen (—183° C.), we may be justified in presuming that when the temperature of the liquid air in the immediate vicinity of the arc rises nitrogen will be given off first, so that the first chemical reaction to start along the arc flash will be one between magnesium vapour and nitrogen. Thus the peculiar character of the magnesium spectrum as observed in the arc under liquid air may be the result of the cooperation of the following factors :—

1. A low temperature keeping down the degree of ionization of the vapours in the arc gap and in this way preventing the formation of a stable arc.
2. Electric forces acting strongly during the first phase and causing emission of spark lines. Feebler electric forces acting during second phase but unable by themselves to keep up strong emission of spark lines.
3. A chemical reaction between nitrogen and magnesium setting in at the end of the first phase and helping (in cooperation with the feebler electric forces) to continue during the second phase the emission of the spark lines initiated by the strong electric forces in the first phase.

§ 7. *Cause of broadening of the hydrogen lines during the first phase. Stark effect.*

From the results of our preliminary experiments we had concluded that the emission of spark lines by the arc depended upon the existence of strong electric fields, and we pointed out that for an electrode distance of 0·05 mm. the intensity of the field set up in the gap with a potential difference of only 110 volts is equal to 22,000 $\frac{\text{volts}}{\text{cm.}}$ *. An electric field of this strength should reveal itself by a manifestation of the Stark effect. As will be remembered, the arc flash is produced between a fixed lower electrode A and an upper movable one B, a drop of liquid (water or oil) being placed between

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* Hemsalech and de Gramont, *loc. cit.* § 12.

them so as to retard arcing. As long as B is in contact with A on striking the arc, the intensity of the field between them is of course zero. But immediately after separation as B moves upwards, a very strong electric field is set up, the intensity of which, however, decreases very rapidly as the distance between A and B increases, and more especially so as soon as arcing has set in after the destruction of the liquid film. Hence we should expect to observe the electric effect whilst the distance between B and A is small, as for example during the first phase. An image of the arc flash composed of the two phases was projected upon the slit of the spectrograph in such a manner that the motion of B took place in a direction parallel to the slit. In this way it was possible to distinguish between the spectrum radiations emitted during the first phase and those given out at later stages of the arc flash. The height of the spectrum thus obtained obviously depends upon the distance AB, namely the length of the arc flash, and that edge of the spectrum which corresponds to the vicinity of A will be emitted whilst the intensity of the electric field is a maximum. We should therefore, on passing down a spectrum line from B towards A, observe a broadening or decomposition of the line analogous to that obtained with Lo Surdo's arrangement*. The liquids which were placed in the arc gap in our experiments contained hydrogen in combination either with oxygen or with carbon, and the spectra show the red and blue lines of the Balmer series. The red line λ 6563 was found to broaden considerably near the edge of the spectrum corresponding to electrode A. The blue line λ 4862 was, however, distinctly decomposed in the first phase, the distance between the components increasing on approaching A ; in fact, this line presented the well-known Eiffel tower-like appearance, so characteristic of the transverse electric effect, as obtained with Lo Surdo's method. The effect is especially well developed and defined in a 200 volt arc between copper or magnesium poles with water films. It shows also in hydrogen and coal-gas. The fact that H_α was only broadened and not decomposed is undoubtedly due to the low dispersion in the red of the glass-prism spectrograph used by us. With the help of Stark's table of data for "Grobzerlegung" † an approximate determination of the intensity of the electric field was made from the amount of maximum separation

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* Lo Surdo, *Rendiconti dei Lincei,* xxii. p. 664 (1913).

† Usabura Yoshida, Memoirs of the College of Science (Kyoto Imperial University) vol. iv. No. 5, p. 188 (1920).

observed for H_β in the water film arc. Thus in the case of a 200 volt water arc between magnesium poles the separation of the outer components of H_β at a distance of about 0·05 mm. from the stationary electrode was found to be 20·3 Ångström units. Hence the shift of each component from the initial line was approximately 10 units. According to Stark an electric field of $10{\cdot}4 \times 10^4 \frac{\text{volts}}{\text{cm.}}$ produces a shift of about 19·4 units for the outer parallel component of H_β. Consequently, since the displacement is proportional to the strength of the electric field, a shift of 10 Ångström units would correspond roughly to $50{,}000 \frac{\text{volts}}{\text{cm.}}$. On calculating the field for a gap of 0·05 mm. with an applied potential of 200 volts we obtain $40{,}000 \frac{\text{volts}}{\text{cm.}}$—a value which is of the same order of magnitude as that derived from the amount of separation of the components through the Stark effect. Thus it would seem that the broadening of the hydrogen lines observed during the initial stages of an arc flash is caused by the strong electric field set up momentarily when the electrodes separate.

§ 8. *Detailed results of observations.*

The photographic records of the spectral phenomena exhibited by electric arcs under various conditions, which served as basis for our measurements and observations, were obtained in the manner already described in § 9 of our first paper. Also the numbers and signs used for expressing relative intensities and characters are the same as those adopted there. For reasons already stated in § 1 we have made a more exhaustive examination of the arc spectra of magnesium. In the case of zinc and cadmium we give the results only for the liquid air and water arc respectively, in addition to that of the ordinary arc. The spectra of these two elements do not play an important rôle in astrophysical problems, and the few results we give will suffice to illustrate the general behaviour of their spark lines under arc conditions.

Most of the photographs were taken on Wratten's panchromatic plates. A few spectra, however, were obtained on ordinary plates and they are therefore deficient beyond λ 5500. In these cases the space in the tables reserved for the relative intensity of the line is left blank. Lines marked S belong to the Rydberg nebulous series, and those marked H to Paschen's series.

Table I.—*Magnesium.*

a. Quartz spectrograph. λ 2150–λ 3200.

Observations were made on the spectra of the direct arc, water arc, and capacity spark. The water arc brings out a series of hazy lines, all well visible and of which the least refrangible one is even fairly strong. These lines had previously been observed only by Kayser and Runge as very feeble lines in the arc. They are absent from the spark.

λλ 2605·3	Fairly well visible.	These lines form part of the 1st nebulous series of triplets; no member of the 2nd series has been observed in this part of the spectrum.
2630·4	Well visible.	
2633·0	Very well visible.	
2668·2	Rather feeble.	
2672·8	Well visible.	
2732·3	Feeble.	
2733·7	Fairly strong.	
2736·7	Fairly strong.	
λ 2777 to λ 2784	A group of lines identical in water arc and spark; in direct ordinary arc, lines are widened and λ 2780 is reversed.	
λλ 2795	Reversed in direct arc and spark, but not in water arc.	
2802		
2852	Doubly reversed in direct arc; simply reversed in water arc.	
2915	Of equal appearance in the three spectra; but the halos are less marked in water arc.	
2928		
2937		
3091	Same in water arc and spark; reversed in direct arc.	
3093		
3096	Same in the three sources.	

b. Uviol spectrograph. λ 3170–λ 5000.

λλ 3330	Intense lines; same in the three sources.	
3332		
3337		
3722	Strong and very hazy in water arc; fairly well seen in direct arc and spark.	Not given in any tables. Two of the lines are marked in the atlas of spectra by Eder and Valenta.
3726	Fairly strong and very hazy in water arc; very feeble in direct arc and spark.	
3732		
3829	Strong and very hazy; same in the three sources.	
3832	Intense and very hazy; same in water arc and spark; reversed in direct arc.	
3838		
3890	Fairly strong and hazy in the three sources.	
3892		
3896		
4058	Strong and sharp in water arc; hazy and feeble in direct arc and spark.	
4168		
4352	Stronger in water arc than in direct arc or spark.	
4481	Very strong in water arc; very feeble in direct arc; intense and expanded in spark.	
4571	Very strong in water arc; only feebly brought out in direct arc and spark.	
4703	Of identical appearance in the three sources.	

The green band at λ 5007 has come out only in the water arc.

c. Glass spectrograph. λ 3600–λ 7000.

Wave-lengths in I. A.	80-volt Arc between Mg poles in Gases and Liquid Air.						Remarks.
	Air.						
	Gaseous.	Liquid.	Nitrogen.	Oxygen.	Hydrogen.	Coal-gas.	
3829·4	8 c	10 c	10 c	8 cr	10 cr	8 cr	
3832·2	10 c	12 c	12 c	10 cr	12 cr	10 cr	
3838·2	15 c	20 c	20 c	15 cr	20 cr	15 cr	
3842·3	—	—	0 dd	—	—	—	
3846·6	—	0 c	½ c	—	—	—	
3847·9	—	—	0 c	—	—	—	
3849·5	½ cn	1 c	2 c	1 cnn	1 cnn	2 cnn	enh.
3854·4	2 cn	3 cbr	5 c	2 cnn	2 cnn	masked by C bands.	enh.
3856·3	—	—	—	—	1 cn		
3890·4	00 c	1 c	1 cs	2 cn	1 cn	1 cn	enh.
3892·0	0 c	2 c	2 cs	3 cn	2 cn	2 cn	enh.
3893·2	—	½ c	½ cs	—	½ cn	00 cn	enh.
3894·1	—	—	—	½ in I 1 cn in II	—	—	
3895·7	½ c	4 c	4 cs	5 cn	3 cn	4 cn	enh.
3898·2	000 c	½ c	½ cs	1 in I 2 cn in II	½ cn	0 cn	enh.
3938·4	—	—	0 cn	—	—	—	
3952·7	—	—	—	—	—	00 c	
3986·9	00 cnn	0 cn	2 cn	—	—	—	S 9
4018·2	—	00 cn	00 c	—	—	—	
4058·3	½ cn	1 cnbr	5 cn	00 cn	0 cn	—	S 8
4167·6	3 cnbr	4 cnbr	8 cn	2 cnbr	2 cnbr	cn blended with line of carbon band.	S 7
4243·1	—	—	0 cn	—	—	—	
4250	000 cn	000 cn	½ cnn	—	—	—	
4323·4	—	—	—	—	—	0 cn	
4352·0	5 cnbr	8 cnbr	10 cn	2 nbr in I 4 nbr in II	4 cnbr	4 cnbr	S 6

4380·6	½ c	½ cs	2 cs	2 c	½ c	1 c	Observed by Fowler and Payne with Mg arc in vacuo.
4385·6	—	—	—	—	0 dnbr	—	
4391·4	—	—	—	—	½ dnbr	1 dd nn	
4429·5	—	—	—	—	0 dnbr	0 d nn	
4436	—	—	—	0 dd nn	½ dnbr	0 d nn	
4481·2	0 at cathode 1 at anode 000 cn in gap	10 cnbrv	4 cs	50 dbrv	50 dnbrv	50 dbrv	enh.
4510·8	—	—	½ c	—	—	—	
4571·1	5 cs	2 cs	8 cs	4 in I 5 s in II	2 cs	3 cs	flame line.
4584·1	—	—	—	0 dd nn	½ dd nn	½ dd nn	enh.
4703·0	10 cnbr	15 cnbr	12 cn	8 cnbr	8 cnbr	8 cnbr	S 5
4730·2	1 c	1 c	5 cs	2 in II only	½ cnn	masked by carbon bands.	
4844·7	—	—	—		0 dnn		red edge of band.
5007·3	5 c	½ c	—	1 in I 8 in II	—	—	red edge of band.
5167·3	6 c	10 c	8 c	8 c	12 cbr	12 cbr	
5172·7	7 c	12 c	10 c	10 c	15 cbr	15 cbr	
5183·6	8 c	15 c	12 c	12 c	20 cbr	20 cbr	
5210·9	—	—	—	—	3 c	2 c	red edge of band.
5218	—	00 cn	00 cn	0 cn	—	0 dn	
5229	—	00 cnn	0 cnn	½ cnn	1 dnn	1 dnn	
5232	—	—	—	—	—	0 dnn	
5242	—	—	00 cn	0 cn	½ dnn	—	
5349	00 c	—	1 cs	—	—	—	
5528·4	½ c	12 cbr	15 c	20 cnbr	15 cnbr	20 cbr	S 4
5566		—	—	—	½ d	masked by carbon band.	red edge of band.
5621		—	—	—	00 c		red edge of band.
5711·3		3 c	6 cs	5 cnbr	3 cbr	5 cbr	
5783·2		—	0 c	—	—	—	H 6
6315·4		000 c	2 c	—	—	—	H 5
6336		—	—	—	0 dd nn	1 dd nn	

Arcs through non-conducting liquids between Mg poles.

Wave-lengths in I. A.	80 volts.				200 volts.		Remarks.
	Ordinary arc.	With drop of			Ordinary arc.	With drop of Water.	
		Water.	Paraffin oil.	Glycerin.			
3829·4	8 c	10 c, r in I	8 c, r in I	8 cr	10 cr	10 c, b^{rv} in I	
3832·2	10 c	12 cr	10 cr	10 cr	12 cr	12 c, b^{rv} in I	
3838·2	15 c	20 cr	15 cr	15 cr	20 cr	20 c, b^{rv} in I	
3846·6	——	——	——	——	000 cn	1 d	
3849·5	½ cn	2 cnn	masked by C bands.	½ cnn	0 cn	2 d, b^{r} in I	enh.
3854·4	2 cn	3 cnb^{r}	masked by C bands.	masked by C bands.	1 cn	4 d, b^{r} in I	enh.
3856·3	——	——	masked by C bands.	½ cnn	——	——	
3890·4	00 c	1 d	1 dn	1 dn	00 c	2 d	enh.
3892·0	0 c	2 d	1½ dn	1½ dn	0 c	4 d	enh.
3893·2	——	——	——	——	——	½ d	
3895·7	½ c	3 d	3 dn	3 dn	1 c	6 d	enh.
3898·2	000 c	½ d	½ dn	½ dn	000 c	1 d	enh.
3945·0	——	——	0 d	——	——	——	
3986·9	00 cnn	——	not seen in I 00 nn in II	——	0 cn	00 cn	S 9
4018·2	——	——	——	——	000 c	00 cn	
4058·3	½ cn	——	00 n in I 2 n in II	0 cn	2 cn	2 cn	S 8
4167·6	3 cnb^{r}	2 nn in I 1 nb^{r} in II	masked by C bands.	2 cn	3 cnb^{r}	5 cnb^{r}	S 7
4250	000 cn	——	——	——	——	000 d	
4352·0	5 cnb^{r}	8 nn in I 4 nb^{r} in II	½ nn in I 10 nb^{r} in II	4 cnb^{r}	6 cnb^{r}	10 cnb^{r}	S 6
4380·6	½ c	——	masked by C bands.	½ c	00 c	1 d	

4391·4	—	—	0 dd nn	—	—	—	
4436	—	—	0 dd nn	000 c	—	00 dd nn	
4481·2	000 cn in gap 0 at cathode 1 at anode	50 dbrv	20 dbrv	15 dbrv	00 at anode 000 at cathode not seen in gap	10 dbrv	enh.
4510·8	—	—	—	—	—	00 d nn	
4571·1	5 cs	3 in I 1 in II	0 in I 4 in II	4 c	6 cs	3 cs	flame line.
4584·1	—	2 dd nn	—	—	—	?	enh.
4651	—	—	—	—	—	00 dd n	
4703·0	10 cnbr	20 in I 10 in II } nbr	1 in I 10 in II } nbr	6 cnbr	10 cnbr	10 cnbr	S 5
4730·2	1 c	? in I 00 in II	masked by C bands.	0 cn	½ c	1 d, b in I	
5007·3	5 c	2 in I 1 in II	— in I 1 in II	3 c	6 c	4 c	red edge of band
5167·3	6 c	10 c	6 c	7 c	10 c	10 c	
5172·7	7 c	12 c	7 c	10 c	12 c	12 c	
5183·6	8 c	15 c	8 c	12 c	15 c	15 c	
5210·9	—	3 in I 1 in II	0 n in I 0 in II	0 in I 00 in II	½ c	1 d	red edge of band
5218	—	—	—	—	—	2 dd n	
5229	—	3 nn in I ½ nn in II	00 nn in I ? in II	—	½ nn at anode	1 dd n	
5232	—	—	—	—	—	1 dd n	
5242	—	2 nn in I 0 nn in II	—	—	—	—	
5252	—	—	—	—	—	1 dd nn	
5349	00 c	—	—	—	3 cs	2 d	
5528·4	½ c	20 cbr	½ in I 1 in II	½ c	15 c	10 c, br in I	S 4
5711·3		4 nn in I 3 n in II			4 at cathode 6 at anode 3 in gap	4 d, br in I	
6315·4		—			000 cnn	00 dn, bv in I	H_β

Arcs through well-conducting liquids.

Wave-lengths in I. A.	80-volt arc between Mg poles.		Arc between graphite poles.			Remarks.
	With drop of Water.	With drop of concentrated solution of Magnesium sulphate.	With drop of concentrated solution of Magnesium sulphate.		With drop of concentrated solution of Magnesium chloride.	
			80 volts.	200 volts.	200 volts.	
3829·4	10 c, r in I	7 cr	6 c, b^{rv} in I	10 in I 4 in II	5 b^{rv} in I 4 cs in II	
3832·2	12 cr	10 cr	8 c, b^{rv} in I	12 in I 6 in II	8 b^{rv} in I 6 cs in II	
3838·2	20 cr	15 cr	12 c, b^{rv} in I	20 in I 8 in II	12 b^{rv} in I 8 cs in II	
3849·5	2 cnn	0 cnn	000 dd nn	½ dd nn	—	enh.
3854 4	3 cnb^{r}	½ cnn	000 dd nn	1 dd nn	—	enh.
3890·4	1 d	½ dn	000 dd n	—	—	enh.
3892·0	2 d	1 dn	000 dd n	000 dd n	—	enh.
3893·2	—	—	000 dd n	—	—	
3895·7	3 d	2 dn	00 dd n	1 dd	—	enh.
3898·2	½ d	0 dn	—	—	—	enh.

4167·6	nn in I 1 nb^r in II	? in I 000 nn b^r in II	00 dd	1 dd n	——	S 7
4352·0	nn in I 4 nb^r in II	? in I 1 nb^r in II	0 c	1 dd	0 dd nn	S 6
4481·2	50 db^{rv}	50 db^{rv}	5 b^{rv} in I 4 c in II	15 db^{rv}	15 b^{rv} in I 4 cs in II	enh.
4571·1	3 in I 2 in II	2 in I 0 in II	——	——	——	flame line.
4584·1	2 dd nn	1 dd nn	——	——	——	enh.
4703·0	20 in I 10 in II } nb^r	6 in I 3 in II } nb^r	1 c, b^r in I	4 nb^r in I 000 in II	½ n in I 000 in II	S 5
5007·3	2 in I 1 in II	——	——	0 dd n	——	red edge of band.
5167·3	10 c	10 c	6 c	8 in I 3 in II	7 in I 5 s in II	
5172·7	12 c	12 c	8 c	12 in I 5 in II	10 in I 7 s in II	
5183·6	15 c	15 c	10 c	15 in I 6 in II	12 in I 8 s in II	
5210·9	3 in I 1 in II	1 in I 00 in II	——	00 dd nn	——	red edge of band.
5229	3 nn in I ½ nn in II	1 nn in I 000 nn in II	——	——	——	
5242	2 nn in I 0 nn in II	——	——	——	——	
5528·4	20 cb^r	20 cb^r	2 in I 1 c in II	6 nb^r in I trace in II	2 in I 00 c in II	S 4
5711·3	4 nn in I 3 n in II	10 in I ½ in II	——	00 dd n	——	

TABLE II.—*Zinc.*

a. Quartz spectrograph. λ 2150–λ 3200.

Sources of light: ordinary direct arc, water arc, and capacity spark.

λλ 2502 } Feeble in ordinary direct arc; strong in water arc and
2558 } intense in spark.

A certain number of lines which are well seen in the spark appear of medium strength in the water arc; they are absent from the ordinary direct arc.

b. Uviol spectrograph. λ 3170–λ 5000.

Sources of light: ordinary direct arc and water arc.

λλ 4630 Very strong in ordinary arc; passing from feeble to fairly strong in water arc.

4912 } Absent from ordinary arc; well seen in water arc;
4924 } characteristic spark lines.

c. Glass spectrograph. λ 3600–λ 7000.

Wave-lengths in I.A.	Ordinary direct arc in gaseous air.	Direct arc in liquid air.	Remarks.
4292·9	1 cs	2 cs	
4629·8	4 cn	10 $\mathrm{cb}^{\mathrm{rv}}$	
4680·1	10 cs	12 $\mathrm{cb}^{\mathrm{rv}}$	
4722·2	10 cs	15 $\mathrm{cb}^{\mathrm{rv}}$	
4810·5	10 cs	20 $\mathrm{cb}^{\mathrm{rv}}$	
4911·7	——	1 dd n	enh.
4924·0	——	2 dd n	enh.
5182·0	2 c	6 cs	
6362·4		20 $\mathrm{cb}^{\mathrm{rv}}$	

TABLE III.—*Cadmium.*

a. Quartz spectrograph. λ 2150-λ 3200.

Sources of light: ordinary direct arc, water arc, and capacity spark.

λλ 2195 Absent from ordinary direct arc; well seen in water arc; fairly strong in spark.

2265 Reversed in ordinary direct arc and in spark; not reversed in water arc.

2288 Intense and reversed in all three sources.

2313 Feeble in ordinary direct arc; strong in water arc; very strong in spark.

2321 Barely visible in ordinary direct arc; fairly strong in water arc; very strong in spark.

2573 } Feeble in ordinary direct arc; strong and sharp in
2749 } water arc; intense in spark.

b. Uviol spectrograph. λ 3170–λ 5000.

Sources of light: ordinary direct arc and water arc.

λλ 3250	Well marked in water arc. absent from ordinary arc; characteristic spark line.	
3526	Strong in ordinary arc; much weakened in water arc; impurity?	
3536	Well marked in water arc; absent from ordinary arc; characteristic spark line.	
3650	Fainter in water than in ordinary arc.	Characteristic arc lines.
3729	Slightly stronger in water arc.	
3982	Well marked in ordinary arc; barely visible in water arc.	
4307	Very well marked in ordinary arc; much weakened in water arc.	
4416	Strong in water arc; absent from ordinary arc; enhanced line.	

The following additional lines undergo no change on passing from the ordinary arc to the water arc: λλ 3253, 3261, 3404, 3466, 3468, 3611, 3613, 3614, 4413, 4662, 4678, 4800, and 5086.

c. Glass spectrograph. λλ 3600–7000.

Wave-lengths in I. A.	Ordinary arc between Carbon cathode and Cd anode.	Water arc between Graphite anode and Cd cathode.	Remarks.
4306·8	8 cn	3 cn, br^{r} in I	
4413·0	8 cs	4 cs	
4415·7	2 cs	5 ds	enh.
46 {14·2 15 4	0 cn	00 cn	
4662·3	10 c	5 cnbr	
4678·2	20 c	12 c, br^{v} in I	
4799·9	20 c	15 c, br^{v} in I	
5085·8	20 c	20 c, br^{v} in I	
5154·7	8 cs	6 c	
5337·9	000 c	2 dd n	enh.
5378·9	00 c	3 dd n	enh.
6325·2	6 cs	3 c	
6438·5	20 c	20 c, br^{v} in I	

§ 9. *Explanation of Plates.*

The reproductions have been made from enlargements of the original photographs. Plate XVII. shows the variations in the character of the spectrum of magnesium in the region comprised by the two triplets λ 3883 and λ 5184 on passing from the ordinary direct arc in gaseous air (*a*) to those under liquid air (*b*), in nitrogen (*c*), and in hydrogen (*d*). All these spectra were obtained with arcs at 80 volts. The photographs show up clearly the remarkable behaviour of the spark line λ 4481 under these various conditions. The relatively great strength and breadth of this line in liquid air and in hydrogen are in marked contrast to its feeble development in air and to its tenuity in nitrogen. The considerable expansion of this line during the first phase of the hydrogen arc is another feature to be noted. Compare also the "winged" lines of the Rydberg series in *a*, *b*, and *d* with the better defined and more perfectly developed lines of the same series in nitrogen (*c*). Further note the relative feebleness of the low-temperature flame line λ 4571 in liquid air and in hydrogen and the symmetrical widening of the blue hydrogen line λ4861 as a result of the Stark effect.

Plate XVIII. gives examples of the effect of liquid films upon various types of magnesium lines. Note the great expansion of the spark line λ 4481 in the first phase of the water arc (*a*) and the strong red wings of the two lines λ 4352 and λ 4703 of the Rydberg series. Remarkable is the great feebleness of these lines during the first phase of the paraffin-oil arc. On the other hand, note the enhancement of the triplet at λ 5184 in the first phase of the same spectrum. Another feature of these three spectra, which were obtained with 80 volt arcs, is the rapid falling off in intensity of the spark line λ 4481 after the end of the first phase.

The first two photographs on Plate XIX. were obtained with a 200 volt arc, *a* being the spectrum of the ordinary arc between magnesium electrodes in air, and *b* that of the same arc with a drop of water between the poles. The most outstanding feature of these two spectra is the extraordinary behaviour of the spark line λ 4481. Hardly perceptible in the ordinary arc, it occupies a position of significant prominence in the water arc not merely by reason of its relative strength, but more particularly on account of its sudden cessation during the second phase whilst all the lines of other types continue to be emitted without any change in intensity. Note the relative weakening of the flame line λ 4571 and the better definition of λ 4352 and λ 4703 of the Rydberg series in the second phase of the water arc. The third photograph (*c*) represents a portion of the ultra-violet region of the magnesium spectrum as given by a capacity spark, water arc and ordinary arc, all taken between electrodes of metallic magnesium. Note the reversals of the flame line of λ 2852.

Plate XX. *a* gives the spark, water arc and ordinary arc spectra of zinc in the ultra-violet region. Note the relative strength in the water arc of the two spark lines λ 2502 and λ 2558, and the strong development in the two arc spectra of the arc line triplet at λ 2801. Spectra *b* and *c* show the relative behaviour in ordinary arc and water arc at 80 volts of the arc line triplet at λ 4811 and of the well-known spark lines λ 4912 and λ 4924. Note absence of latter in the ordinary direct arc (*b*).

Photograph *a* on Plate XXI. is a portion of the ultra-violet region of the spark, water arc and ordinary arc spectra of cadmium. Noteworthy are the relative behaviour in the three sources of the spark lines λλ 2195, 2313, and 2321 and the curious reversals of λ 2288. Spectrum *b* shows the abrupt drop in intensity of the enhanced line λ 4416 at about the middle of the second phase of a water arc, whilst its neighbour, the arc line λ 4413, continues to be visible and dies out only gradually. The behaviour of this enhanced line is similar to that of the spark line of magnesium λ 4481 illustrated on Plate XIX. *b*.

§ 10. *Discussion of results.*

The experiments described in this paper, together with those related in our first communication, go to show that the emission of light radiations in an electric arc is governed by a number of factors which generally act simultaneously and thereby complicate the task of tracing the origin of any particular spectrum lines. By means of new experimental methods it has been possible to bring out distinctly the effects of that factor which is more directly responsible for the emission of spark lines. Our preliminary work with lead and tin had led us to the conclusion that the excitation of these lines is connected with the existence of strong electric fields, and it will therefore be necessary in the first place to examine with the help of all the data now to hand whether and in how far this conclusion was justified. As we have shown, the spark lines attain their maximum of development as regards both intensity and breadth during the first phase—namely, within about 0·0001 second from the moment of separating the electrodes. They continue to be emitted after arcing has set in, and then fall off sharply in intensity or stop quite abruptly before the end of the second phase. Further, the spark line λ 4481 is continuously emitted by a stable arc burning in nitrogen. Thus a satisfactory explanation of the emission of spark lines in the arc must account for the following facts :—

(1) The emission of spark lines in the first phase ;
(2) their symmetrical broadening, especially during the first phase ;
(3) their abrupt cessation before the end of the second phase.
(4) The emission as a sharp narrow line of λ 4481 by a stable arc in nitrogen.

Let us first consider the case of the water arc at 80 volts. With this low voltage no spark will leap across the electrodes through the water however small the distance between them be made, for, as is well known, the dielectric strength of a medium increases as the pole distance decreases. Thus, at very small distances the electric field acting between the poles can be made very great. If, for example, the distance between the electrodes is 0·05 mm.—namely, equal to about one-half the thickness of the water film at the end of the first phase,—the acting electric field would be 16,000 $\frac{\text{volts}}{\text{cm.}}$. But the electric fields set up in this way maintain their high values only so long as no discharge passes between the electrodes, and with the establishment of an arc the intensity of the acting field would immediately descend to a much smaller value. Let us now follow the course of events when an arc is struck by bringing the electrodes into contact. Whilst the electrodes are touching, the intensity of the electric field between them is of course zero. But at the instant of their separation a very powerful electric field is suddenly brought into operation which, up to a pole distance of 0·05 mm., lasts only for about 0·00005 second on account of the rapid upward motion of the top electrode, as explained in § 4. Now this short space of time is about the same as the duration of the second phase of a powerful condenser discharge with an initial electric field of about 20,000 $\frac{\text{volts}}{\text{cm.}}$ (pole ends 2·5 mm. radius and 10 mm. spark gap), so that it is quite conceivable that also the average drop of potential along the path of the current in the two cases (arc and spark) will have approximately equal values. We should therefore expect the characters of the spectra emitted by these two sources to be similar. This inference is completely borne out by the results of our observations. For not only are the spark lines predominant during the first phase of the water arc but they are also symmetrically widened, which is precisely one of their characteristic features in the capacity spark. There is, however, a further striking similarity between the spectra given by the capacity spark and the first phase of a water arc—namely, the character of the hydrogen lines is the same. In both sources the lines of the Balmer series are considerably broadened. As is well known, these lines are narrow and sharp with slow discharges under low potential gradients, such as the ordinary coil discharge through a vacuum tube or the self-induction spark through hydrogen at atmospheric pressure *.

With regard to the rôle played by the liquid films, the results of our experiments with electrolytes have shown clearly that they do not act as dielectrics. It seems to us more probable that they merely serve to retard the formation of the arc flash and in this way allow the electric field, which becomes momentarily established between the electrodes, to attain values comparable to those obtained in a capacity spark.

Thus, not only the particular state of the electrical conditions arising from our special experimental arrangement, but also the observed character of both hydrogen and metal lines point to the existence of strong electric fields during the first phase of a water arc. This conclusion seems to be strongly supported by our observations of the decomposition of the H_β line by the electric field, as recorded in § 7. The value of the electric field as derived from the amount of displacement of the outer components was found to be in good agreement with that obtained by direct calculation, so that the existence of strong electric fields during the initial stages of an arc flash appears to be highly probable. A further fact in support of this contention seems to be provided by the peculiar behaviour of the lines of the Rydberg series of magnesium. These lines are strongly broadened towards the red during the early stages of a water arc, but they appear without wings in a stable arc in nitrogen with an electric field of only about 150 $\frac{\text{volts}}{\text{cm.}}$. Now, as Messrs. Takamine and Kokubu have shown †, these lines are precisely displaced towards the red in a strong electric field. As we have further shown, the spark line λ 4481, which is symmetrically broadened during the first phase of a water arc with a strong electric field, appears as a very narrow line in the

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* Hemsalech, *Comptes Rendus de l'Académie des Sciences*, t. cxxix. p. 288 (1899).

† Takamine and Kokubu, Memoirs of the College of Science (Kyoto Imperial University), vol. iii. p. 178 (1918).

nitrogen arc with a feeble electric field. We therefore venture to suggest that *the symmetrical broadening of the spark line* λ 4481 *and the red wings of the lines of the Rydberg series observed during the first phase of a water arc are a manifestation of the Stark effect.*

Since both the emission and the character of the spark lines are independent of the nature of the liquid used, we have no hesitation in assuming that the explanation which we have given for their origin in the water arc holds equally good for arcs with paraffin oil, alcohol, glycerin, etc. Further, as we have already shown in § 6, the emission of spark lines at the instant of striking an arc in a gaseous medium without the intervention of a liquid film may be most satisfactorily explained by assuming the transitory existence between the poles of a rarefied space caused by the rapid recession of the upper electrode. By temporarily preventing chemical reactions between the metal vapour and the gases of the medium this rarefied space would, like the liquid films, retard the formation of the arc and thus permit the momentary establishment of high potential gradients along the path of the discharge.

We now proceed to consider the course of events during the second phase of an 80 volt water arc. This phase begins at the instant of destruction of the water film, and the distance between the electrodes is then 0·10 mm. Thus the intensity of the applied electric field at this moment is only 8000 $\frac{\text{volts}}{\text{cm.}}$. As the arc gap further increases the electric field diminishes and the spark line λ 4481 is observed to grow narrow very rapidly until, at a pole distance of 1·51 mm., there occurs an abrupt and considerable drop in its intensity. At this point the value of the applied electric field is down at 528 $\frac{\text{volts}}{\text{cm.}}$. After this event the spark line shows only very feebly, dying out gradually; the arc flash, however, continues and comes to an end when the tip of the movable electrode has reached a distance of 4·76 mm. from the stationary one, corresponding to an applied field of only 168 $\frac{\text{volts}}{\text{cm.}}$. In order to see whether there is any connexion between the acting electric field and the emission of spark lines during the second phase, it is necessary to compare the values of the applied fields at the moment of the abrupt cessation of the intense emission of these lines under various electrical and other conditions. For, if the emission of spark lines is really governed by electric forces, it seems plausible to assume that such an important event as the sudden stopping of their radiations must be an indication that a certain critical value of the electric force has been reached below which these lines are no longer excited by this means. In the following table are given the values of the applied electric fields at the moment of the abrupt falling off or sudden stoppage of the spark line λ 4481. These values have been computed from the data given in §§ 4 and 5. It should be specially remarked that they do not represent the drop of potential along the path of the arc flash at the particular moment considered, but only the intensity of the electric force which would prevail if the resistance of the arc were infinitely great. The arc flashes were passed between poles of magnesium metal, except where otherwise stated.

	Nature of source.	Intensity of applied electric field.	Remarks.
80 volt arcs.	Glycerin	840 $\frac{\text{volts}}{\text{cm.}}$	Carbon bands strongly developed.
	Paraffin oil	770 ,,	
	Water	528 ,,	
	Concentrated solution of magnesium sulphate between Mg poles	478 ,,	
	Same between graphite poles	519 ,,	Carbon bands not seen.
	Hydrogen	519 ,,	
	Blown arc	404	
200 volt arcs.	Water	462 ,,	
	Concentrated solution of magnesium chloride between graphite poles	834 ,,	Carbon bands absent but calcium lines predominant.

As will be seen, the majority of the figures obtained for λ 4481 are in the neighbourhood of 500 $\frac{\text{volts}}{\text{cm.}}$, and it may be useful to examine more closely those cases which differ widely from this average value—namely, the glycerin arc, the paraffin oil arc, and the arc with a drop of magnesium chloride solution between graphite poles. Our photographs of the spectra of the first two cases reveal the fact, by reason of the very strong development of the carbon bands, that the electric current was largely carried by carbon vapour, which is a good conductor. Hence the drop of potential along the arc flash will of necessity be low on account of the low resistance of the vapour, and the point at which the critical value of the electric force for λ 4481 is reached will be situate nearer to the stationary pole than in an arc of greater resistance. Since our calculations take no account of the prevailing resistance they will, in an arc of high conductivity, lead to values which are too great. In the case of the magnesium sulphate arc between graphite poles the carbon bands do not show in the spectrum, and, accordingly, the value found for the electric force, namely 519 $\frac{\text{volts}}{\text{cm.}}$, is near the average. In the third case, magnesium chloride between graphite poles, the spectrum of the arc shows also no trace of the carbon bands, but its predominant feature is the strong development of the lines and bands of calcium. Now it is well known that an arc passes particularly well through calcium vapour, and therefore the latter must be a good conductor of electricity. Hence we venture to ascribe the high value obtained in this case for the applied electric force to the presence of calcium vapour which lowered the resistance of the arc. Thus it would seem that all our values are to some extent influenced by the resistance prevailing in the arc. Our lowest value, namely 404 $\frac{\text{volts}}{\text{cm.}}$, for the blown arc would therefore indicate that this arc possessed the highest resistance of all the arc flashes examined; this inference seems likely to be true, since air was blown through the arc from the commencement till the end of the flash. As a result of these considerations, we venture to conclude that *the emission of the spark line* λ 4481 *is controlled by electric forces and, further, that there exists a definite critical minimum value of this force below which this particular radiation is no longer excited.*

With regard to the permanent emission of λ 4481 in a stable arc burning in nitrogen, it is evident that the electric forces alone would not suffice to cause its excitation, since the average value of the acting electric field was only about 150 $\frac{\text{volts}}{\text{cm.}}$. Nor can the higher temperature of the stable arc account for it, because the line shows only the merest traces along the path of a stable arc in air and no sign of it has been detected at the very high temperature prevailing in the fringe zone of a single plate resistance furnace. But, as we have already suggested in § 5, it is quite possible that the emission of λ 4481 by a nitrogen arc is brought about by the chemical reaction between the magnesium vapour and the surrounding gas. Since, however, this line is not emitted in the explosion region of the air-coal gas flame, where a similar reaction occurs, it would seem that in the case of the arc in nitrogen the emission is finally realized with the help of the additional effects of the higher temperature and of the prevailing electric forces.

§ 11. *Summary.*

1. The emission of spark lines during the first phase of a liquid film arc is independent of the nature of the liquid. Further, the liquid film does not play the rôle of a dielectric since a well conducting electrolyte acts in the same way. § 2.

2. The raising of the voltage of the arcing current prolongs the life of the spark lines during the second phase and, in the case of magnesium, brings into prominence the lines of the Rydberg series. § 3.

3. A remarkable behaviour is shown by the spark line λ 4481 of magnesium. The emission of this line either falls off quite suddenly in intensity or stops abruptly at a definite point during the second phase, as though some factor, absolutely essential for its excitation, had suddenly ceased to act or reached some critical minimum value below which it is no longer capable of stimulating this particular radiation. It is shown that this critical point corresponds to an applied electric field of approximately 500 $\frac{\text{volts}}{\text{cm.}}$. §§ 3 and 10.

4. The striking behaviour of the 3rd and 4th type enhanced lines of cadmium has disclosed the interesting fact that during the gradual decline of the acting electric forces the character of the spectrum changes quite abruptly at several definite stages, as though the radiating centres concerned were at these points undergoing sudden modifications in their structure. § 4.

5. Measurements of the thickness of the liquid film at the end of the first phase together with an estimate of the speed of the upward moving electrode have shown that some of the phenomena occurring during the early stages of the first phase are of the same order of duration as the oscillation stage of a capacity spark in which spark lines are so strongly emitted. § 4.

6. An explanation has been offered to account for the flashing up of the spark lines at the instant of striking the arc in various gaseous atmospheres. It is suggested that, as the upper electrode moves away from the stationary one, a vacuous space is momentarily left between them through which the initial stages of the arc discharge take place. In this way the electric field set up is enabled to develop its effect before any appreciable chemical reaction has set in between the vapours and the surrounding gas. § 5.

7. A stable arc is obtained between magnesium poles in an atmosphere of nitrogen showing λ 4481 as a sharply defined

line. Further, the lines of the Rydberg series form a prominent feature of the spectrum. It is suggested that the emission of λ 4481 and the more pronounced appearance of the lines of the Rydberg series are partly caused by the chemical reactions involved in the formation of magnesium nitride. § 5.

8. The spark line λ 4481 is brought out prominently in an arc burning under liquid air and its emission takes place evenly along the whole path of the flash. Under similar conditions the spark lines of zinc show strongly only during the first phase. § 6.

9. Experiments and observations are described which seem to indicate that the broadening of the hydrogen lines H_α and H_β observed during the early stages of an arc flash is caused by the strong electric field set up momentarily when the electrodes separate. § 7.

10. A determination of the intensity of the electric field set up during the first phase of a water arc made from the amount of displacement of the outer components of H_β has given a value which is in good agreement with that obtained by direct calculation. § 7.

11. Detailed results are given of observations of the spectra of magnesium, zinc, and cadmium under various arc conditions. Reproductions of photographic records secured in the course of this research illustrate the relative behaviour and the characteristic features of various types of lines. §§ 8 and 9.

12. A discussion of our results with particular reference to the line λ 4481 of magnesium has led us to the conclusion that its emission during the first phase of a liquid or vacuous film arc is connected with the momentary establishment of a strong electric field between the electrodes. The further suggestion is made that the symmetrical broadening of this line and the expansion towards the red of the lines of the Rydberg series, which are observed under these same conditions, are manifestations of the Stark effect. § 10.

§ 12. *Concluding remarks.*

The fact that spark lines or so-called high temperature lines are brought out prominently in an arc when the vapours of the latter are cooled, and that they disappear, on the other hand, when the temperature is raised, should help to remove the last doubts as to the futility of using these particular spectrum lines for the estimation of the temperature prevailing in a source of light. Further, the emission by the

Bunsen cone of such characteristic arc lines as the magnesium triplets λ 3838 and λ 5184, and their absence from the hottest part in the mantle of the same flame, are results which go far to emphasize the necessity for exercising the greatest caution in selecting spectrum lines for the purpose of establishing a temperature classification of the stars. The relative sensitiveness of the various types of magnesium lines to electric and chemical actions is brought out in the following table (p. 870), which has been constructed with the help of data obtained in the course of the present research and of those resulting from observations by Messrs. Hartley and Ramage [*], de Watteville [†], King [‡], and Hemsalech [§].

It will be seen from this table that the only types of magnesium lines emitted in the absence of electric or special chemical actions are the flame line λ 4571 and the series triplets. But whereas the former is apparently not affected by electric actions, the triplets, on the contrary, show marked increase in brightness as the intensity of electric actions rises. Also the special chemical actions prevailing in the inner cone of the air-coal gas flame bring the triplets into prominence already at a temperature which by itself would be unable to excite them. Hence, if in a source of light the triplets are observed to be very intense as compared with the line λ 4571, we must suspect the presence of chemical or electric actions in that source. The electric actions, as has been shown by one of us [‖], may be relatively feeble, provided the metal vapour be at a high temperature. If, however, the source of light emits in addition to these two types of lines also those of the Rydberg series and the spark line, then, as our table indicates, the electric actions must be of a much more vigorous kind than in the first case. Should the spark line λ 4481 appear symmetrically broadened and the lines of the Rydberg series winged on the red side, it is most probably an indication that an electric current flows through the source or part of it at a high potential gradient under the action of a powerful electric field. The temperature of the vapour in the source may in this case be relatively low. If, on the other hand, λ 4481 be a sharp narrow line, relatively feeble as compared with the triplets and the lines of the Rydberg series, and if, further, the lines of the latter be fairly well defined, it

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[*] W. N. Hartley and H. Ramage, Trans. Royal Dublin Soc. ser. 2, vol. vii. p. 343 (1898–1901).

[†] C. de Watteville, Phil. Trans. Roy. Soc. A. vol. 204. p. 151 (1904).

[‡] A. S. King, Astrophysical Journal, vol. xlviii. p. 79 (1918).

[§] G. A. Hemsalech, Phil. Mag. vol. xl. p. 307 (1920).

[‖] G. A. Hemsalech, *loc. cit.*

Predominant mode of excitation *.		Flame line λ 4571.	Series triplets λ 3838 and λ 5184.	Rydberg's Nebulous series.	Spark line λ 4481.
	1. *Without external electric field.*				
Thermo-chemical ...	Mantles of air-coal gas flame; temp.=1850° C.	Predominant.	Absent.	Absent.	Absent.
	Mantles of oxy-hydrogen flame; temp.=2500° C.	Fairly strong.	Strong.	Absent.	Absent.
	Mantles of oxy-acetylene flame; temp.=2700° C.	Fairly strong.	Strong.	Absent.	Absent.
Chemical	Cone of air-coal gas flame; temp. about 1700° C.	Fairly strong.	Strong.	Absent.	Absent.
	2. *Feeble electric fields.*				
Thermo-chemical and Thermo-electrical.	Electric tube resistance furnace; field about 0·5–2 $\frac{\text{volts}}{\text{cm.}}$.	Strong.	Strong.	Uncertain.	Absent.
Thermo-electrical ...	Fringe of single plate resistance furnace; field from 6–8 $\frac{\text{volts}}{\text{cm.}}$.	Relatively feeble.	Strong.	Absent.	Absent.
	3. *Moderately strong electric fields.*				
Thermo-electrical ...	Ordinary electric arc in air; field about 70–200 $\frac{\text{volts}}{\text{cm.}}$.	Relatively feeble.	Strong.	Fairly strong and nebulous.	Traces only.
Thermo-electrical and Chemical......	Ordinary arc in nitrogen; field about 150 $\frac{\text{volts}}{\text{cm.}}$	Relatively feeble.	Strong.	Very prominent and lines better defined.	Relatively feeble but sharply defined.
	4. *Fairly strong electric fields.*				
Thermo-electrical ...	Second phase of liquid and vacuous film arcs; fields 500 $\frac{\text{volts}}{\text{cm.}}$ and over.	Relatively feeble.	Strong.	Strong, sometimes diffused and winged.	Strong, and fairly narrow.
	5 *Strong electric fields.*				
Electrical	First phase of liquid and vacuous film arcs; fields over 10,000 $\frac{\text{volts}}{\text{cm.}}$.	Relatively feeble.	Very strong.	Strong, and winged on red side.	Very intense and symmetrically broadened.
Electrical	Oscillation stage of capacity spark; fields of over 10,000 $\frac{\text{volts}}{\text{cm.}}$.	Relatively feeble.	Very strong.	Strong, and winged on red side.	Very intense and symmetrically broadened.

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* G. A. Hemsalech, Phil. Mag. vol. xxxvi. p. 294 (1918).

may be concluded that the source emitting this spectrum is the seat both of moderately strong electric forces and of some special chemical actions. The temperature of the vapours in this case would be higher than in the preceding one.

Thus it is evident that if we wish to draw any conclusions with regard to the agents at work in a source of light, we must not be guided merely by the fact that certain types of lines are present or predominate in its spectrum, but we should pay special attention to the character of the lines. Further, it should be necessary to take into account the presence of certain gases, such as hydrogen or nitrogen, and note the character of their spectrum lines or bands. And last, but not least, notice should be taken as to whether the luminous phenomenon observed is permanent or only transitory with rapid spectral changes; for we have seen that the effects of intense electric fields are most strongly brought out in the early stages of development of a light source (arc or spark) when the temperature and the conductivity of the vapour are still low. As the temperature increases, that emission which depends upon the presence of a high potential gradient diminishes or even vanishes. Thus, it would be dangerous to conclude that a star possesses a high temperature merely because spark lines predominate in its spectrum, and such a conclusion would be specially difficult to maintain in the case of the early stages of development of a new star or Nova.

Manchester and Paris,
July 1921.

XCV. *Young's Modulus and Poisson's Ratio for Spruce.* By H. Carrington, *B.Sc., M.Sc.Tech., A.M.I.Mech.E.*[*]

[Plate XXII.]

PREVIOUS research on the elasticity of timber has extended over many species, but has been almost entirely confined to the determination of values of Young's Modulus along the grain[†]. The only values of Poisson's Ratio which appear so far to have been published are a few for pine, box, and beech, by A. Mallock[‡].

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[*] Communicated by the Author.

[†] Todhunter and Pearson, 'The Theory of Elasticity.' Unwin, 'The Testing of Materials of Construction.' Johnson, 'The Materials of Construction.' S. J. Record, 'The Mechanical Properties of Wood.' W. H. Baring, 'Timber: Its Identification and Mechanical Properties' (The Royal Aeronautical Society, London, 1918).

[‡] Proc. Royal Society, vol. xxix. (1879).

The determination of the elastic properties for a particular species of timber presents some difficulty, for treated—as it should be—as having three planes of elastic symmetry, nine elastic constants are required, completely to define its elastic properties, whereas an isotropic material such as steel requires only two. The problem is further complicated by the fact that the æolotropy of the material is variable, which has to be reckoned with in an investigation on its elasticity.

Before the advent of the aeroplane a knowledge of the elasticity of timber was seldom required in practical problems. When, however, it began to be used extensively in aeroplane construction, information about its elasticity became both desirable and necessary. A research on the elastic properties of spruce was accordingly undertaken by the author during the war, in the College of Technology, Manchester, for the Air Board and Royal Aircraft Establishment, and the following paper gives the results of the investigation to determine values of Young's Modulus and Poisson's Ratio.

The results were obtained on the assumption that each piece of spruce experimented upon had three planes of elastic symmetry. All the test pieces were accordingly cut so far from the pith of the tree that the annual layers of the portion of each piece over which the strains were measured were sensibly plane surfaces. The portion could thus be considered as having three planes of symmetry of structure, which were treated as planes of elastic symmetry.

The largest pieces experimented upon were 13 inches long, about 1 in. wide and $\frac{1}{4}$ in. thick, the dimensions of the smaller pieces being approximately in proportion. The values of Young's Modulus and Poisson's Ratio were obtained from measurements of the principal curvatures of the neutral surfaces when the pieces were bent by couples suitably applied to their ends[*]. Considering the case of a large piece, this rested upon knife-edges 12 inches apart, and the load was applied equally to two other knife-edges, 8 inches apart and symmetrical with respect to the outer knife-edges. The bending moment between the inner knife-edges was thus constant, and the neutral surface was a surface of anticlastic curvature[†]. From measurements of the principal

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[*] Phil. Mag. Feb. 1921.

[†] Thomson & Tait, Nat. Phil., Arts. 711–718.

curvatures of this surface the values of Young's Modulus and Poisson's Ratio were deduced. The curvatures were obtained from measurements of the slope of the surface in the planes of the principal curvatures. In the case of the curvature of flexure, this was deduced from the slopes at the ends of a 1 in. length symmetrically situated with respect to the central normal cross-section and the knife-edges. Also the curvature in the plane of the central normal cross-section was obtained from measurements of the slope near the edges of the beam. Actually the load was increased by equal amounts and the slopes measured after every increase. The slopes were then plotted against the load, and from the slopes of the resulting lines the curvatures, and thence the elastic constants, were calculated.

In addition to the elastic constants, the elastic limit stress and modulus of rupture were recorded for each test piece. The elastic limit was calculated using the value of the couple corresponding with the point where the load-curvature line ceased to be straight. The modulus of rupture was taken as equal to the stress at the elastic limit, multiplied by the ratio of the breaking couple to the couple at the elastic limit.

The timber experimented upon was obtained from the R.A.E. in 1915 in the form of four large balks, which represented the good average type of spruce which was available for aeroplane manufacture early in the war. The balks will be denoted by the letters A, B, C, and D, and a photograph of the end of balk A is reproduced in fig. 1 (Pl. XXII.). Micro-photographs of normal, axial, and tangential sections for balk A, magnified about 40 diameters, have previously been published *.

All these photographs are typical of the remaining three balks. The balks were straight grained and free from knots and shakes, and were well seasoned before the test pieces were prepared from them.

In the notation used in the paper, the direction of the grain is denoted by ZOZ, the direction perpendicular to this and normal to the annual layers by XOX, and the direction perpendicular to both the above, which is thus tangential to the annual layers, by YOY. The symbols E_x, E_y and E_z are used to denote Young's Modulus in the direction XOX, YOY, and ZOZ respectively. Also the symbols σ_{yz}, σ_{zy},

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* Phil. Mag. June 1921.

σ_{zx}, σ_{xz}, σ_{xy}, and σ_{yx} denote Poisson's Ratio where

$$\sigma_{yz} \ldots\ldots = \frac{\text{lat. strain in the direction ZOZ}}{\text{long. strain in the direction YOY}}.$$

The following six types of experiments were performed:—

Type 1. Length in direction XOX, breadth in direction YOY, thickness in direction ZOZ, giving values of E_x and σ_{xy}.

Type 2. Length in direction XOX, breadth in direction ZOZ, thickness in direction YOY, giving values of E_x and σ_{xz}.

Type 3. Length in direction YOY, breadth in direction XOX, thickness in direction ZOZ, giving values of E_y and σ_{yx}.

Type 4. Length in direction YOY, breadth in direction ZOZ, thickness in direction XOX, giving values of E_y and σ_{yz}.

Type 5. Length in direction ZOZ, breadth in direction XOX, thickness in direction YOY, giving values of E_z and σ_{zx}.

Type 6. Length in direction ZOZ, breadth in direction YOY, thickness in direction XOX, giving values of E_z and σ_{zy}.

In addition to the constants, the elastic limits, and moduli of rupture, the following properties were measured for each test piece:—The density when tested, density dry, humidity, shrinkages in directions XOX and YOY, and the number of annual rings per inch. Each piece was dried immediately after testing in an electrically heated oven at 104 degrees centigrade for from 24 to 48 hours, and then carefully weighed and measured. This enabled the humidity, shrinkages, and dry densities to be obtained. The humidity and shrinkages were calculated as percentages on the weights and dimensions respectively of the dry test pieces, the humidity being taken as

$$\frac{\text{Weight when tested} - \text{Weight when dry}}{\text{Weight when dry}} \times 100.$$

All the results are tabulated in Table I.

It will be noted that about 10 experiments of each type were performed for each balk, and that the means of the results are tabulated. Also columns are included showing the probable variation from the mean of each property.

These were obtained on the assumption that the properties obeyed the laws of probability, and Peter's formula * was used to calculate them.

TABLE I.

Baulk	Type of Exp:	No. of Expts	Density dry lbs/cu ft	Probable variation from mean %	No. of annual rings per in.	Probable variation from mean %	Moisture per cent	Probable variation from mean %	Shrinkage in direction XOX (per cent)	Probable variation from mean %	Shrinkage in direction YOY (per cent)	Probable variation from mean %	Ratio of shrinkages $\frac{YOY}{XOX}$	Probable variation from mean %	Young's Mod (E) 10^4 lbs per sq. in.	Probable variation from mean %	Poisson's Ratio (σ)	Probable variation from mean %	Elastic Limit lbs per sq. in.	Probable variation from mean %	Mod. of Rupture lbs per sq. in.	Probable variation from mean %	Mod. of Rupture / Elastic Limit	Probable variation from mean %
A	1	9	22·9	1·05	17·8	12·5	12·2	6·7	1·86	8·6	3·77	6·7	2·04	5·2	10·4	7·6	0·571	3·7	257	2·80	881	2·95	3·47	4·6
	2	10	23·3	1·65	17·0	15·0	11·2	4·5	1·72	4·2	3·10	6·6	1·82	4·1	11·2	4·1	0·0315	28·5	244	11·0	895	5·6	3·82	16·0
B	1	8	31·0	0·40	13·5	8·7	11·1	8·1	2·92	5·9	3·66	5·8	1·24	3·6	11·4	3·3	0·427	5·9	303	40·0	869	25·0	3·08	16·1
	2	10	30·9	1·45	21·8	3·5	10·3	6·1	2·43	7·2	3·03	6·8	1·25	5·0	12·2	18·0	0·0182	29·0	299	18·8	955	7·2	3·44	20·0
C	1	10	27·3	1·80	9·0	9·5	11·8	7·5	2·27	5·6	3·77	4·8	1·66	5·1	11·4	5·7	0·515	6·9	300	8·7	1120	9·7	3·73	9·0
	2	11	27·1	1·40	8·7	4·5	10·3	6·3	1·80	8·5	3·02	11·0	1·69	4·9	13·1	9·0	0·0308	20·0	332	10·0	1140	4·5	3·53	9·8
D	1	8	24·3	0·50	12·3	13·0	12·8	9·0	2·12	5·9	4·43	5·7	2·09	6·9	10·3	6·0	0·638	7·6	253	9·0	893	5·6	3·64	14·5
	2	8	24·3	1·00	12·5	13·0	11·2	2·3	1·72	10·0	3·53	11·7	2·03	7·5	9·29	15·4	0·0287	43·5	250	7·9	1010	8·0	3·36	3·9
A	3	9	23·0	3·5	20·7	27·0	11·8	4·0	1·90	7·4	3·39	6·5	1·83	6·2	6·05	8·7	0·290	11·7	147	10·0	636	4·3	4·27	8·7
	4	3	22·9	3·0	13·4	13·2	10·2	5·6	1·96	10·8	3·18	6·5	1·64	5·5	6·16	9·7	0·0133	46·2	191	11·2	518	9·7	2·73	8·7
B	3	10	30·5	1·40	17·4	6·0	12·0	4·5	2·77	5·2	3·60	6·9	1·30	4·1	9·06	4·6	0·335	6·9	190	16·3	1040	6·4	5·75	14·2
	4	10	30·7	2·20	17·5	13·2	12·1	4·3	2·80	7·1	3·40	5·0	1·18	6·9	9·39	4·7	0·0233	28·0	236	14·6	888	7·0	3·01	12·6
C	3	10	26·6	3·9	6·9	7·8	11·7	6·2	1·95	5·3	3·51	6·5	1·80	3·3	8·09	6·6	0·311	5·9	191	12·8	740	6·5	4·23	10·0
	4	10	26·9	3·2	7·65	5·2	11·7	2·75	2·23	6·9	3·42	4·3	1·57	6·5	9·02	30·0	0·0253	26·2	236	18·2	665	19·4	2·93	12·3
D	3	9	24·4	1·35	13·0	25·6	10·0	2·50	1·82	5·3	3·56	5·6	1·92	4·2	5·91	5·3	0·317	8·4	115	12·4	544	6·5	4·77	9·2
	4	10	24·6	1·10	13·9	19·7	11·0	1·20	1·89	5·8	3·76	4·0	2·00	4·0	7·02	10·4	0·0165	21·0	200	8·0	503	13·5	2·60	8·3
A	5	10	23·2	3·30	17·4	41·0	11·7	9·5	1·87	6·1	3·31	4·6	1·76	6·3	1·38	8·2	0·436	11·6	4340	3·3	9300	4·9	2·10	2·70
	6	10	23·6	2·85	16·8	27·1	12·4	3·8	2·16	7·1	3·60	5·0	1·71	4·4	1·49	4·1	0·561	11·1	5630	4·0	10700	1·85	1·88	5·2
B	5	9	31·6	2·90	23·8	8·7	14·0	1·8	3·33	4·0	3·72	6·7	1·13	6·9	2·44	7·0	0·364	12·8	7010	6·3	—	—	—	—
	6	10	31·1	3·8	23·5	13·7	13·0	0·95	3·32	7·1	3·78	2·85	1·15	6·6	2·41	6·5	0·520	6·5	8270	8·8	15500	5·5	2·03	8·4
C	5	9	27·7	1·70	11·5	24·3	12·8	3·0	2·41	5·6	3·94	7·5	1·63	4·7	1·86	5·1	0·384	9·7	5230	10·0	11700	3·8	2·38	11·0
	6	9	26·9	4·8	10·2	35·4	12·5	1·80	2·40	6·7	3·96	4·3	1·67	6·2	2·11	18·0	0·509	4·4	6990	24·0	12480	13·0	1·85	12·0
D	5	9	24·6	1·30	9·8	25·3	14·2	5·1	2·24	5·5	4·17	5·9	1·30	7·9	1·82	3·5	0·386	13·3	5400	10·3	10700	7·0	1·87	15·5
	6	9	24·6	2·15	10·4	3·3	13·2	2·35	2·06	10·5	4·15	4·0	2·04	7·7	1·78	3·9	0·485	5·8	5810	6·0	10650	7·7	1·34	7·1

Type 1. gives values of E_x, σ_{xy}, Elastic Limit and Modulus of Rupture in direction XOX
- - - 2 - - - - - - - E_x, σ_{xz}, - XOX
- - - 3 - - - - - - - E_y, σ_{yx}, - YOY
- - - 4 - - - - - - - E_y, σ_{yz}, - YOY
- - - 5 - - - - - - - E_z, σ_{zx}, - ZOZ
- - - 6 - - - - - - - E_z, σ_{zy}, - ZOZ

For description of type of experiment see page 874.

The above procedure was adopted because appreciable differences in the values of the properties were often evidenced for pieces which had been nearly adjacent to each other in a balk. Reasons for this seemed to be accounted for by variations in the structure of the test pieces which were often visible when they were examined under the microscope, and it was considered sufficient to treat the variations as characteristic of the structural nature of the material, and to take the means of the properties as representative of the balk.

It will be noted from the tables that the humidity or moisture contents of all the pieces are sensibly the same, that is about 12 per cent.

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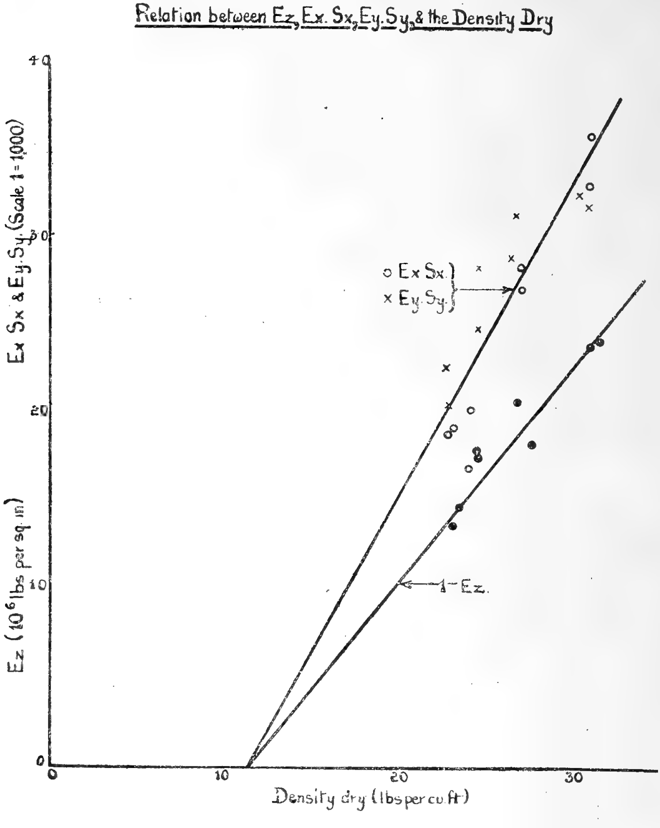
* 'Theory of Errors and Least Squares.' Weld, New York, 1916.

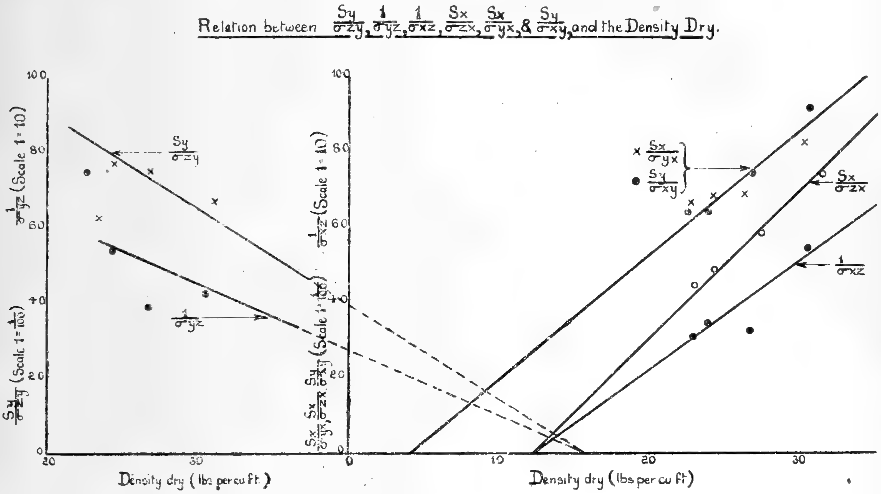
Although no connexion between the properties for a particular balk could be found, it seemed probable that relations might exist between the means of the properties corresponding with each balk. A consideration of the table of results resulted in the curves shown in figs. 2 and 3.

Fig. 2.



Here S_x and S_y denote the shrinkages in the direction XOX and YOY respectively per unit length of dry timber, corresponding with 12 per cent. of moisture. Referring to fig. 2, it will be noted that the relation between E_z and the dry density is linear, also that the relation between E_xS_x, E_yS_y, and the density dry is represented by one straight line. Further, these lines intersect on the abscissa. Similar relations are shown to exist in fig. 3 between values of Poisson's Ratio, the shrinkages, and the dry densities. All the points lie sufficiently near to the straight lines except those corresponding with σ_{zy} and σ_{yz}, but it should be observed that these values were obtained from pieces which were cut with their thicknesses in the direction XOX, that is in the direction of the widths of the rings. The thicknesses of the pieces were thus often comparable with widths of the rings, so that the ratio of Autumn wood to Spring wood usually varied from piece to piece.

Fig. 3.



It is significant to note in connexion with these curves that they all obey the symmetrical relations of n, an æolotropic body having three planes of elastic symmetry *. These relations are :

$$\frac{\sigma_{yz}}{E_y}=\frac{\sigma_{zy}}{E_z}, \quad \frac{\sigma_{zx}}{E_z}=\frac{\sigma_{xz}}{E_x}, \quad \frac{\sigma_{xy}}{E_x}=\frac{\sigma_{yx}}{E_y}.$$

From an examination of the curves it will be found that approximately these equalities are equal respectively to 700 S_y, 700 S_x and $\frac{S_y}{S_x}$.

The degree of accuracy aimed at throughout all the experiments was an error of less than one per cent. It should, however, be noted that in all cases except where the length of the pieces was in the direction of the grain, incipient creeping was evidenced at comparatively small

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* Love's Elasticity, Art. 73.

strains. It was therefore decided to load all the specimens at such a rate that the rate of longitudinal straining on surfaces $\frac{1}{8}$ inch from the neutral surface was approximately at the rate of 1 in 4000 per minute.

The author wishes to thank the former Principal J. C. M. Garnett, M.A., D.Sc., for providing facilities for conducting the research, and Professor Gerald Stoney, F.R.S., for the interest he has shown throughout.

XCVI. *The Diurnal Periodicity of Earthquakes.*
By Charles Davison, *Sc.D.*[*]

THE present paper may be regarded as a sequel to two earlier papers dealing with the same subject. In 1896, I applied the method of harmonic analysis to seismographic records obtained in Japan, the Philippine Islands, and Italy[†]. The results showed a distinct diurnal period, with its maximum-epoch about noon, except in two of the nine Italian records when the maximum-epoch occurred about midnight. In the early after-shocks of Japanese earthquakes, the maximum-epoch was also about or shortly after midnight. Returning recently to the subject[‡], I was able to avail myself of more numerous and extensive records of Japanese earthquakes, and found, by the method of overlapping means[§], that, in ordinary Japanese earthquakes, the maximum-epoch of the diurnal period occurred at or shortly before noon, and that of the semi-diurnal period at 8 or 9 A.M. and P.M.; while, in after-shocks, the epoch of the diurnal period was at first about or shortly after midnight, returning later to the neighbourhood of noon.

Since the latter paper was written, I have applied the same method to the registers collected by the Seismological Committee of the British Association[||]. As the instruments providing these registers are capable of recording earthquakes from very distant regions, it might be expected that, if the maximum-epoch at every place were to occur at a constant local time, the result would be a marked diminution in the amplitude of the diurnal periodicity. In some registers this may be the case; the amplitude is so small, or the variations in the twelve-hourly means are so irregular, that the existence

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[*] Communicated by the Author.

[†] Phil. Mag. vol. xlii. pp. 463–476 (1896).

[‡] *Loc. cit.* vol. xli. pp. 903–916 (1921).

[§] *Boll. Soc. Sism. Ital.* vol. iv. pp. 89–100 (1898). See also "A Manual of Seismology" (Camb. Univ. Press, 1921), pp. 185–188.

[||] As a rule, the registers at my disposal end with the year 1912.

of the periodicity is uncertain. In others, the period is very distinct, the amplitude of the diurnal period at Trinidad and Christchurch (N.Z.) being about 80 per cent. of the mean hourly number of earthquakes. In the following Tables I have included only those results which seem to me free from doubt.

In Tables I. and II. the time at which the preliminary tremors were first recorded is taken as the time of occurrence of the earthquake. The maximum-epoch is thus retarded, but by an amount that is certainly less than the time required by the tremors to travel from the most distant origin. In measuring the amplitude, the mean hourly number of earthquakes is taken as unity. In the column headed $\sqrt{\pi/n}$, n is the number of earthquakes included in the record. Unless the amplitude obtained from isolated records exceeds the value of $\sqrt{\pi/n}$, the result, as Prof. A. Schuster has shown [*], must be regarded as doubtful. If, however, the epochs obtained for the six winter months (October to March, in the northern hemisphere) agree with those for the six summer months (April to September), the doubt is lessened or removed, even if the amplitudes should fall below the corresponding values of $\sqrt{\pi/n}$.

Diurnal Seismic Period.

In Table I. are given the periodic elements deduced from 17 records divided into three groups. Those obtained from the catalogue of local earthquakes at Tokyo are added for comparison. It will be seen that, with one exception (Baltimore), there is a close agreement in the epochs for the winter and summer months.

Thus, in nine records, the maximum-epoch of the diurnal period occurs about noon ; in three, about midnight ; and in five others (three of them in India) early in the afternoon. At Baltimore, the maximum-epoch for the winter months occurs at 1 A.M., and for the summer months at 1½ P.M. Other examples of this reversal will be given later.

Semi-Diurnal Seismic Period.

The number of records giving satisfactory results for the semi-diurnal period is small. In those which are excluded here, the amplitude is usually close to the value of $\sqrt{\pi/n}$ and the series of six-hourly means vary somewhat irregularly. The results obtained for local earthquakes at Tokyo are added for comparison. (Table II.)

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[*] Roy. Soc. Proc. vol. lxi. pp. 455–465 (1897).

Table I.—Diurnal Seismic Period.

Record.	Whole year.			Winter.			Summer.		
	Epoch.	Ampl.	$\sqrt{\pi/n}$.	Epoch.	Ampl.	$\sqrt{\pi/n}$.	Epoch.	Ampl.	$\sqrt{\pi/n}$.
Shide	11 a.	·13	·04	11 a.	·13	·06	1½ p.	·13	·05
Kew	noon	·32	·05	1½ p.	·30	·07	noon	·36	·07
Paisley	noon	·35	·07	1½ p.	·20	·10	noon	·54	·10
Valetta	ab. 10 a.	·20	·08	10½ a.	·33	·11	...	...	...
Batavia	11 a.	·16	·05	11 a.	·19	·07	10½ a.	·14	·07
Tokyo	1 p.	·43	·06	1½ p.	·58	·08	1 p.	·27	·08
,, (local earthquakes)	11 a.	·08	·04	noon	·06	·05	11 a.	·10	·05
Trinidad	ab. 1 p.	·79	·09	2½ p.	·77	·13	noon	·98	·12
Toronto	1½ p.	·13	·05	2½ p.	·13	·08	ab. 0½ p.	·16	·08
Cape of Good Hope	noon	·13	·07	11 a.	·17	·10	...	...	...
San Fernando	1 a.	·28	·05	1½ a.	·33	·07	midn.	·25	·07
Baltimore	ab. 11 p.	·19	·08	1 a.	·36	·10	1½ p.	·20	·14
Cordova (Argentine Republic)	midn.	·57	·06	midn.	·69	·08	1 a.	·46	·09
Calcutta	5 p.	·22	·06	4 p.	·16	·09	3½ p.	·28	·09
Bombay	2 p.	·19	·07	2 p.	·13	·09	1 p.	·25	·09
Madras	ab. 3 p.	·11	·06	2 p.	·08	·09	1½ p.	·16	·09
Honolulu	4 p.	·30	·06	3½ p.	·33	·09	3½ p.	·28	·08
Christchurch (N.Z.)	4 p.	·82	·08	4 p.	·77	·11	3½ p.	·90	·11

Table II.—Semi-Diurnal Seismic Period.

Record.	Whole year.			Winter.			Summer.		
	Epoch. A.M. & P.M.	Ampl.	$\sqrt{\pi/n}$.	Epoch. A.M. & P.M.	Ampl.	$\sqrt{\pi/n}$.	Epoch. A.M. & P.M.	Ampl.	$\sqrt{\pi/n}$.
Valetta	9	·21	·08	9	·27	·11	9	·16	·12
Tokyo	11½	·13	·06	12	·27	·08	10	·14	·08
,, (local earthquakes)	8½	·10	·04	8½	·13	·05	8½	·06	·05
Trinidad	11	·41	·09	10½	·35	·13	11	·46	·12
Baltimore	11	·27	·08	9½	·30	·10	9	·21	·14
San Fernando	1½	·29	·05	1½	·30	·07	1½	·29	·07
Cordova	3	·32	·06	3	·41	·08	1	·30	·09

Thus, in four records, the maximum-epoch of the semidiurnal period occurs at about 9 to 11 A.M. and P.M.; and, in two, at about $1\frac{1}{2}$ to 3 A.M. and P.M. In the latter, the maximum-epoch of the diurnal period occurs at about midnight.

Diurnal Periodicity in relation to Intensity.

If the origin of seismic periodicity be due to causes which precipitate, rather than produce, the occurrence of earthquakes, we should expect to find the periodicity more marked with weak, than with strong, earthquakes. In many of the records considered in this paper, it is possible to make a rough classification of the earthquakes according to intensity. The earthquakes in the diagrams of which a maximum can be clearly distinguished are not of necessity strong, but among them are included all strong earthquakes. Those which contain no marked maximum are, as a rule, of much less intensity. In Tables III. and IV. the lines marked A give the results for the maximum-epochs of the earthquakes recorded, those marked B give the results for the initial tremors when no maximum can be detected.

The following results may be deduced from Table III.:—

(i.) With one exception (Victoria, B.C.) the amplitude of the diurnal period is much greater in the weak, than in the strong, earthquakes.

(ii.) In the strong earthquakes, the maximum-epoch occurs about noon at Shide, Kew, Edinburgh, San Fernando, and Cape of Good Hope; about midnight at Toronto and Victoria, B.C.; and in the afternoon at Cordova. The midnight maximum at Shide in summer may be accidental, as the amplitude is not much in excess of the expectancy.

(iii.) In the weak earthquakes, the maximum-epoch occurs about noon at Shide, Kew, Toronto, Victoria, B.C., and Cape of Good Hope; about midnight at San Fernando and Cordova; at Edinburgh, it occurs about noon in winter and shortly before midnight in summer.

(iv.) There is thus an inversion of epoch in strong and weak earthquakes at San Fernando, Toronto, and Victoria, B.C.; a partial inversion at Edinburgh and Cordova; and a general correspondence in epoch at Shide, Kew, and the Cape of Good Hope.

TABLE III.—Diurnal Seismic Period in relation to Intensity.

Record.		Whole year.			Winter.			Summer.		
		Epoch.	Ampl.	$\sqrt{\pi/n}$.	Epoch.	Ampl.	$\sqrt{\pi/n}$.	Epoch.	Ampl.	$\sqrt{\pi/n}$.
Shide	A	11 a.	·05	·04	ab. noon	·08	·05	1 a.	·08	·05
	B	0½ p.	·39	·07	0½ p.	·39	·10	1 p.	·41	·10
Kew	A	ab. 1 p.	·16	·07	2 p.	·17	·09	noon	·17	·09
	B	1 p.	·43	·07	2 p.	·41	·11	noon	·49	·10
Edinburgh	A	11 a.	·08	·05	ab. noon	·11	·07	11 a.	·06	·06
	B	10 p.	·16	·09	11 a.	·19	·13	10 p.	·36	·12
San Fernando	A	ab. 11 a.	·11	·06	ab. 11 a.	·14	·09	11 a.	·09	·09
	B	1 a.	·77	·08	1½ a.	·83	·11	0½ a.	·72	·11
Toronto..................	A	ab. 0½ a.	·16	·08	ab. 0½ a.	·16	·11	ab. 11 p.	·16	·11
	B	1½ p.	·30	·07	0½ p.	·27	·10	ab. 0½ p.	·36	·11
Victoria, B.C.	A	ab. 11 p.	·17	·08	ab. 9½ p.	·22	·11	ab. 11 p.	·19	·11
	B	10 a.	·11	·07	11 a.	·19	·10	...	·13	·11
Cape of Good Hope...	A	1 p.	·17	·07	1 p.	·19	·10	1 p.	·16	·10
	B	noon	·25	·13	...	...	...	...	...	...
Cordova..................	A	5 p.	·23	·09	6 p.	·27	·12	ab. 2 p.	·20	·13
	B	0½ a.	·90	·08	0½ a.	1·02	·10	1 a.	·79	·12

TABLE IV.—Semi-diurnal Seismic Period in relation to Intensity.

Record.		Whole year.			Winter.			Summer.		
		Epoch. A.M. & P.M.	Ampl.	$\sqrt{\pi/n}$.	Epoch. .M. & P.M.	Ampl.	$\sqrt{\pi/n}$.	Epoch. A.M. & P.M.	Ampl.	$\sqrt{\pi/n}$.
San Fernando	A	$3\frac{1}{2}$	·06	·06	$5\frac{1}{2}$	·08	·09	$3\frac{1}{2}$	·08	·09
	B	$1\frac{1}{2}$	·54	·08	$1\frac{1}{2}$	·46	·11	$1\frac{1}{2}$	·62	·11
Bombay	A	$2\frac{1}{2}$	·08	·07	ab. 2	·06	·10	$2\frac{1}{2}$	·16	·10
	B	ab. 9	·19	·15	...	...	...	...	...	...
Toronto	A	$4\frac{1}{2}$	·16	·08	$4\frac{1}{2}$	·13	·11	$4\frac{1}{2}$	·19	·11
	B	$2\frac{1}{2}$	·13	·07	$2\frac{1}{2}$	·21	·10	$1\frac{1}{2}$	·06	·11
Victoria, B.C.	A	$4\frac{1}{2}$	·08	·08	$4\frac{1}{2}$	·17	·11	2	·10	·11
	B	1	·14	·07	1	·21	·10	2	·17	·11
Cape of Good Hope...	A	12	·08	·07	9	·14	·10	12	·14	·10
	B	12	·13	·13	...	...	...	...	...	...
Cordova	A	$5\frac{1}{2}$	·13	·09	5	·14	·12	$6\frac{1}{2}$	·21	·13
	B	3	·51	·08	3	·49	·10	1	·57	·12

It is worth while noticing that somewhat similar results are obtained for the annual period of shocks of different intensities (Table IV.). In strong shocks, the maximum-epoch is nearly always in winter. There appear, however, to be two distinct classes of slight shocks, one with the maximum-epoch in winter and the other in summer. Of the two classes, the former probably contains the stronger shocks, for the winter maximum is manifested by the less complete of two catalogues for the same district; while the summer maximum is only visible in the results obtained from the fullest records or from catalogues in which the very slightest shocks are included [*].

Thus, with one exception (Toronto), the amplitude of the semi-diurnal period is greater in weak, than in strong, earthquakes. Except at Bombay, there is no evidence of any inversion, or considerable change of epoch.

Origin of the Diurnal Periodicity of Earthquakes.

In Japan the diurnal periodicity of ordinary earthquakes may be due to more than one cause; that of after-shocks is probably due to the diurnal variation of barometric pressure [†] The effects of the latter variation will no doubt depend on the mode of origin of the earthquakes. If the ordinary earthquakes were due to slips along a normal fault, the maximum-epoch of seismic frequency should coincide approximately with that of barometric pressure. If they were due to slips along a reversed fault, the maximum-epoch of seismic frequency should coincide approximately with the minimum-epoch of barometric pressure. Lastly, if the ordinary earthquakes were due to slips along a reversed fault, the after-shocks would be caused by returns of the displaced mass towards its former position of equilibrium, and thus the diurnal variation in pressure (with a maximum shortly after midnight) would cause the maximum-epoch of ordinary earthquakes to occur about noon, and that of after-shocks about midnight. In this way, we may account in part perhaps, but not entirely, for the curious reversal of maximum-epoch manifested in several of the above records.

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[*] Phil. Trans. 1893 A, pp. 1116–1120.

[†] Phil. Mag. vol. xli. pp. 915–916 (1921).

XCVII. *On Atoms and Molecules.* II.

By ALBERT C. CREHORE *.

PART I.

Models of the Lighter Elements.

THE intended order of presentation of this subject begun in a previous paper † has been modified because of developments that seem important. Part I. of the present paper is devoted to a description of the concrete forms that the atoms of the lighter elements assume in conformity with the views given in the first paper. The subject of the radiation of energy from such atoms in both light and X-ray form, which was promised to follow this paper, is deferred in order to present a phase of the subject that may eventually prove to be of practical value to the chemist.

It has been found, so far as we have gone, that the atoms described under Part I. unite with each other to form molecules just as they are known to do by experience. The computation of the forces exerted by one atom upon another is begun in Part II. The forms of the atoms representing helium and neon will neither combine with hydrogen nor with themselves, and there is good reason to know that they cannot combine with any other atoms, although manifestly specific examples of their combination with all elements have not been made.

A reproduction from a photograph of the atomic models is shown in fig. 1. This will be better understood by referring to the diagram of the hydrogen atom given in the first paper, supposed to have a positive charge of two units with very small dimensions situated in between two negative electrons. The same diagram will equally well represent the alpha particle if the single positive charge of two units is replaced by a single charge of four units, the two negative electrons being retained, thus making the whole charge of the alpha particle equal to plus two.

In making the several references to the recent experimental work of Rutherford, which occur below, it seems proper to state that all of these models in fig. 1 had actually

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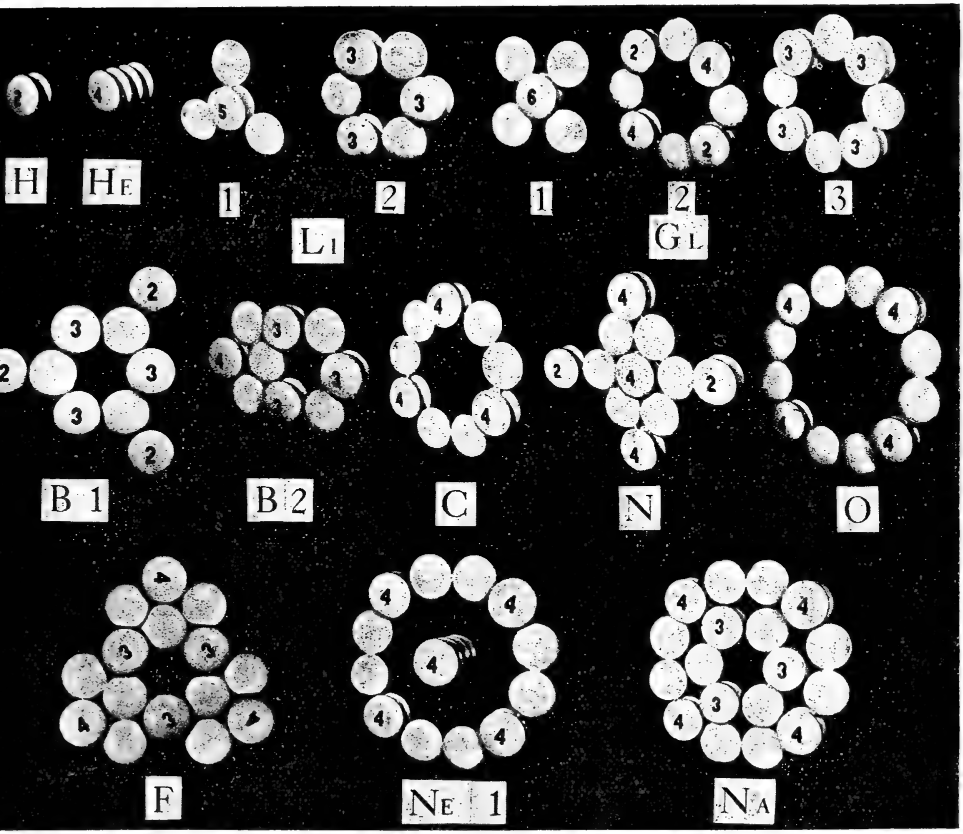
* Communicated by the Author.

† Phil. Mag., October 1921, p. 569.

been constructed at a time before his work was known to the writer.

It is not supposed, as Rutherford has done, that the positive charge of all atoms is composed of aggregates of the positive charge of the hydrogen atom ; but it is supposed* that there exist positive bodies or charges as individual separate entities having the values 2, 3, 4, 5, and 6 units, that is these multiples of the electron's charge. The masses attributed to these individual positive charges are considered to be constant wherever they occur and are given in Table I. in terms of oxygen as 16.

Fig. 1.



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* See Note added in February 1922 at end of Part I.

TABLE I.

Positive charge.	Mass.
$2e$	1·008
$3e$	7/3
$4e$	4·
$5e$	6·
$6e$	9·

These numbers proceed almost but not quite in accordance with the squares of the charge on the supposition that a charge of plus e, if it has any existence, would be one quarter of 1·008, or 0·252. To follow this rule exactly would result in the fractional numbers, 1·008, 2·268, 4·032, 6·300, and 9·072. The fractions have arbitrarily been dropped in each instance except in the cases of $2e$ and $3e$, which latter is retained as 2·333 instead of 2·268. The numbers on the models of fig. 1 represent the number of units of charge of a positive individual, which in each instance is contained within a volume too small to see in a model, and located in between two electrons in an obscured position, as in the diagram of hydrogen referred to.

To consider the various atoms in detail, helium is represented as a pile of four negative electrons bound together by a single positive charge of $4e$ located between the central pair of electrons. The nucleus of this atom may be considered to be the alpha particle, consisting of a single positive charge of four units with two negative electrons in contact with it, the two outside electrons of the He-atom being those that become detached during radiation. This is much the same as Rutherford's form for helium, except that he makes the positive charge four hydrogen positive charges, or four hydrogen ions so-called, which would have a mass of 4·032 instead of 4, unless they each differ from their value in hydrogen. Another important exception is that the two outside electrons are supposed to be situated a long distance away from the centre of the atom by Rutherford, though what it is that holds them in such positions is somewhat of a mystery. A still more important difference is that here a definite shape and location is assigned to each of the charges making up the atom. The major diameter of the negative electron, calculated in the first paper, is

$$2a_0 = 6{\cdot}514 \times 10^{-13} \text{ cm.}$$

and the minor diameter

$$2b = 2{\cdot}130 \times 10^{-13} \text{ cm.},$$

their ratio being 3·058, the same as for the positive charge. It is interesting to note that the diameter of the negative electron obtained experimentally by Rutherford falls between these values, namely $3{\cdot}5 \times 10^{-13}$ cm. This may well be a kind of mean between the figures above given. It would make a difference how the electron is oriented when hydrogen gas is bombarded with alpha particles. Collision might occur at a distance of 6·5, and again it might not occur until the distance is reduced to $2{\cdot}13 \times 10^{-13}$ cm.

The next atom, lithium, has been investigated by Aston * and found to have two isotopes, the one with mass 6 and the other with mass 7. The accuracy claimed for these values is within about one part in one thousand. The isotope of mass 7, Li–No. 2 in fig. 1, is represented as a ring or hexagon, in which the positive individuals are arranged in an equilateral triangle, each having two electrons, one on either pole as in the hydrogen model or in the alpha particle. There are also three connecting electrons to hold the system together located in the same circle with the positive charges, that is on the equator. These electrons approach very close to but do not touch the adjacent electrons occupying planes above and below them. They are each attracted toward the doublet because it has an effective charge of $3-2=1$. The mass of this isotope is exactly $3 \times \frac{7}{3} = 7$, if according to Table I. the mass of the positive charge of three is 7/3.

The other isotope of Li, namely Li–No. 1 in fig. 1, has but a single positive charge of 5 units † situated in the centre of the only doublet, and is surrounded by an equatorial ring of three single electrons. The mass of the charge of 5 is 6 according to Table I., so that this form satisfies this requirement. The official weight given for Li is 6·94, indicating that the isotope No. 2 is of the more frequent occurrence.

The next atom, glucinum also called beryllium, has not yet been investigated experimentally for isotopes, so far as known to the writer, but its official weight, 9·1, indicates that isotopes are probable. The scheme followed here enables one to construct possible forms of the isotopes of Gl, and it will prove of interest if the masses corresponding to the forms shown are later obtained experimentally. In

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* Phil. Mag., May and November 1920.

† See Note, p. 894.

analogy with Li one may suppose that two isotopes of Gl are as in fig. 1, Gl 1 and Gl 3, both being based upon a square instead of a triangle form. This, however, makes the masses 9 and $9\frac{1}{3}$, the latter being a value with a large fraction. If the positive charges of three units in this form are changed into two twos and two fours, two hydrogen atoms being on one diagonal and two alpha particles on the other, as in Gl 2 fig. 1, the mass is 10·016 instead of $9\frac{1}{3}$. These three forms are shown tentatively for Gl.

The atom of boron* is known to have two isotopes of masses 10 and 11 respectively. The form, B–No. 2, of mass 11 is obtained by the addition of one alpha particle and two equatorial electrons to the second isotope of Li, giving the mass $7+4=11$.

There is an opportunity to add two more such alpha particles and connecting electrons around the Li–No. 2 hexagon. The addition of one makes the mass 15, and corresponds to no known element, but the addition of two makes the mass 19 and is represented by the very symmetrical assemblage shown at F fig. 1, as fluorine. There are no isotopes of fluorine as yet found.

A possible configuration for boron is shown as B–No. 1 in fig. 1, consisting of the Li hexagon to which three hydrogen atoms are attached, thus forming a very symmetrical figure of mass 10·024.

In this connexion it is interesting to note that nitrogen and these less stable isotopes of boron and glucinum are the only atoms shown in fig. 1 that have hydrogen as one constituent. Rutherford has succeeded in obtaining hydrogen from nitrogen in the gaseous form; but, in trying several compounds of nitrogen in the solid form, he noted that boron nitride and para-cyanogen gave between 1·5 and 2 times the number of hydrogen atoms to be expected. The experimental result is in agreement with the supposition that hydrogen may have been obtained from this isotope No. 1 of boron, as has been recognized by Rutherford, who says: "In the case of boron nitride there is also the uncertainty whether boron itself emits H atoms." According to this form of model the question is answered in the affirmative, that boron does contain hydrogen.

The atom of carbon takes a very symmetrical form, consisting of a ring of 9 having three positive units of four each in equilateral triangle formation. The mass is thus exactly 12, there being no isotopes; but an important

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* *Loc. cit.*

difference between carbon and the preceding atoms first makes its appearance in that there are two connecting electrons instead of a single one between the doublets containing the positive individuals The connecting electrons do not remain in the equatorial plane exactly, but are staggered the one up and the next down alternating all the way around. This feature is not shown in the model.

The oxygen atom is very similar to carbon, but differs in being based upon a square of positive charges instead of an equilateral triangle. There are also double connecting electrons as in carbon. The mass is exactly 16, there being no isotopes.

The only remaining atom in the second row of the periodic table is nitrogen. This differs materially from the ring form of carbon and oxygen, and has an alpha particle at its exact centre surrounded by a hexagon of single electrons, which are supposed to be staggered alternately up and down out of the equatorial plane. The circumference outside of this hexagon contains two alpha particles and two hydrogen atoms, and the whole figure has two planes of symmetry. The mass is $3 \times 4 = 12$ plus $2 \times 1{\cdot}008 = 2{\cdot}016$, making a total of 14·016, thus agreeing with remarkable accuracy with the official weight of nitrogen, 14·01, which has been determined with as much or more care than any other element.

The next element, neon, has two isotopes at least, one of mass 20 and the other 22. The form, Ne–No. 1 fig. 1, is thought to be made by the addition of a helium atom in the centre of the oxygen ring, the five alpha particles having a mass 20. The isotope of this, 22, not shown in fig. 1, is thought to consist of the same atom to which is added two hydrogen atoms, one on either pole of the central helium atom, thus making a pile of three coaxial atoms in the centre of the oxygen ring, one helium atom and two hydrogen atoms.

The next element, sodium, has no isotopes as yet found and an exact weight of 23. It falls under Li in the periodic table, and is thought to consist of the hexagon isotope of Li of mass 7 within the oxygen ring of mass 16, thus making up the total mass 23.

This is as far as we shall attempt to go at the present time, although considerable interest attaches to the elements immediately following, Mg, Al, Si, P, S, and Cl, to complete the third row in the periodic table. Of these, Mg, Al, Si, and Cl are known to have isotopes.

The work of Rutherford in the disintegration of nitrogen and oxygen will immediately occur to the reader, because he has apparently found that one of the products of disintegration of both nitrogen and oxygen is a new atom having a mass of three.

Since there is no provision in the above plan for any atom with mass 3, it seems to be required that the experimental result of Rutherford be reconciled with the views here expressed. And, accordingly, a close study of this question has been made. When the two hydrogen atoms are knocked off from the nitrogen atom, the whole atom no doubt receives such a shock that some of the electrons are driven away at the same time. Those most easily dislodged are the ones concerned in the process of light radiation, namely one of the pair composing the doublets in contact, that is, with the positive charge, as is shown in a subsequent paper on radiation. It seems probable that what is left of the nitrogen atom after the loss of the hydrogen may be the collection of charges shown in fig. 2, consisting of three positive individuals of charge 4 each together with seven binding electrons. There are no doublets in fig. 2 as in the models, the positive charges being attached at the end of the minor axes of single electrons as in the hydrogen ion, which on this view has one electron and one positive charge of two units. The total charge of

Fig. 2.

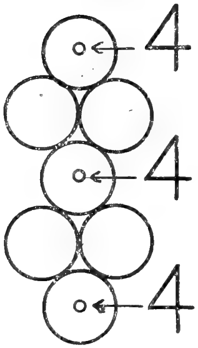

Fig. 3.

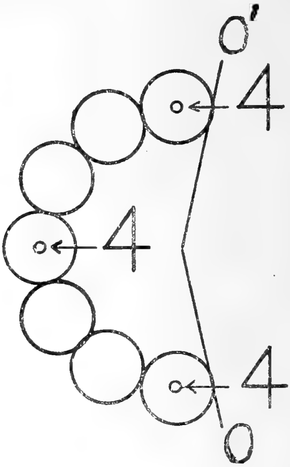

Fig. 2.—A possible residue when the nitrogen atom is disintegrated.

Fig. 3.—A possible residue when the oxygen atom is disintegrated. This is the same combination of charges as in fig. 2, and no doubt rearranges itself into a different form, possibly that of fig. 2.

the residual atom is, therefore, $12-7=5$ units, and the total mass is 12.

In considering the breaking up of the oxygen ring it may be supposed that it is cut in two along the line OO′ indicated in fig. 3. This will leave a portion which, however, will have lost one electron from each doublet, and thus the number of electrons left is 7 and the positive charge is 12 and mass 12, namely, exactly the same combination as obtained from nitrogen above. The geometrical form cannot remain as a portion of a ring on account of the repulsion of the two ends, and seems likely to adjust itself to exactly the same more stable form of fig. 2.

In going over the calculations of Rutherford * undertaken for the purpose of finding the mass of the unknown atom from his observations, it is found that he has begun with an assumption not experimentally well substantiated, that the unknown atom carried a charge of two units. If, for the moment, it be granted that this charge might possibly have been five units, then the ratio of the charge E′ of the unknown atom to the known charge $E=2$ of the alpha particle, which ratio now becomes 5/2 instead of unity, will have to be carried all through the subsequent work. Doing this results in the equation

$$1{\cdot}14\,\mathrm{MVE}' = 1{\cdot}25\,mu\mathrm{E},$$

instead of his equation (1). Combining this with his formula (2), which will remain unchanged, results in the values for the unknown atom:

$$\begin{aligned} m &= 12{\cdot}1, \\ u &= 0{\cdot}76\,\mathrm{V}, \\ \text{and} \quad x &= 9\text{ cm.} = \text{the observed range.} \end{aligned}$$

It does not seem a safe procedure to base deductions upon the original energy of the alpha particle and assume that this is the only energy available because, if the energy is sufficient to break up the atom, there becomes available another source of energy which must affect the velocities of the parts of the atom, the residue, and this energy is now unknown. Thus the unknown mass comes out 12 instead of 3 and is in agreement with the conception that this unknown atom is the residue from both nitrogen and oxygen, having a charge of 5 units. The percentage 121/120 is a little closer agreement than that found by Rutherford as 31/30, though this is of little moment. If the above turns out to be a

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* Bakerian Lecture, 1920, Proc. Roy. Soc. ser. A, vol. xcvii. No. A 686, p. 390.

possible interpretation to place upon the experimental observations of Rutherford, it shows that the unknown atom may have been that of fig. 2 obtained from both nitrogen and oxygen during its disintegration.

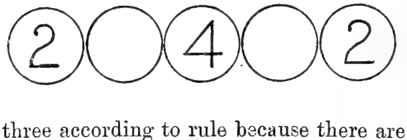
The exact agreement between Rutherford's result for nitrogen and the model shown for N is truly astonishing when it is borne in mind that he has found experimentally that the distance from the centre of the N atom to the centre of the H atoms in nitrogen is just two diameters of the electron itself. The reason why there has been found to be a critical experimental distance within which the law of scattering suddenly changes is made apparent by this theory. Also the reason why the hydrogen atoms are driven ahead without much scattering within this critical distance is because two electrons, the one in the hydrogen atom and the other in the alpha particle, come into actual collision and cannot interpenetrate each other.

Note added February 1922.

Since the manuscript of this paper was submitted in August 1921 experimental results of importance have been published. A rule has been adopted for determining the atomic number of the atom from the models which necessitates some changes in fig. 1. The rule may be stated as follows:—the atomic number is equal to the total number of connecting electrons in the atom, provided one is counted for hydrogen and two for helium, and that one be counted in the more complex atoms when a single doublet, that is either a hydrogen atom or an alpha-particle, occupies the exact centre of the atom, and that two is counted when a helium atom occupies the centre.

According to this rule the models shown as Li–1, Gl–1 and B–1 in fig. 1 do not have the proper atomic numbers for these elements, but all of the others satisfy this rule. The charges of $5e$ and $6e$ with masses of 6 and 9 respectively in accordance with Table I. are thus never required. A new model for Li–1 having perfect symmetry about its centre is shown in fig. 1 *a*, having mass $4+2\times1{\cdot}008=6{\cdot}016$, and

Fig. 1 *a*.



atomic number three according to rule because there are two connecting electrons and an alpha-particle at the centre for which one is to be counted, making three. The isotope Li–2 of fig. 1 may remain as the principal isotope of Li having mass 7, for it satisfies the rule giving atomic number three.

G. P. Thomson* reports glucinum as an atom of mass 9, and states

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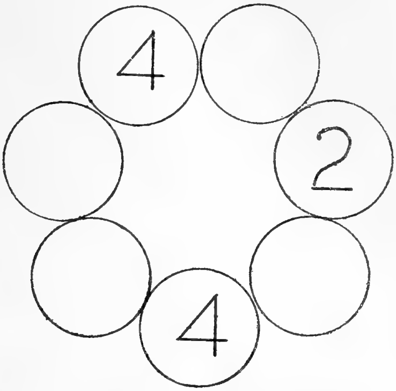
* Phil. Mag. Nov. 1921, p. 859.

that if there is an isotope of mass 10 or 11 its existence is not established by his investigation. A new model for Gl is shown in fig. 1 *b*, this

Fig. 1 *b*.



being simply the octagon ring shown at Gl–2, fig. 1 with one of the hydrogen atoms missing. The atomic number is four according to rule and mass $2 \times 4 + 1 \cdot 008 = 9 \cdot 008$.

The form shown for boron at B–2 fig. 1 gives mass 11 and atomic number 5 according to rule, but it may be rejected because of its unsymmetrical form, and also because boron probably contains hydrogen as recently observed by Rutherford. The preferred form for boron is the octagon ring Gl–2 of fig. 1 in which a single hydrogen atom is inserted at the exact centre. This raises the mass from 10·016 to 11·024 and the atomic number from 4 to 5 according to rule. It supplies an atom rich in hydrogen, containing three H-atoms, and is symmetrical.

The atomic weight of boron has recently been revised from 11·0 down to 10·9 in the latest International Table since the work of Aston on isotopes. It seems possible that the isotope of 10 found by Aston may be the octagon form shown as Gl–2 fig. 1 having mass 10·016, which may enter the boron as an impurity. Its atomic number is 4 rather than 5 and should be classed as Gl, though it is very similar to the boron atom.

Rutherford has recently obtained great range particles from B, N, F, Na, Al, and P. He does not state that all of these particles are hydrogen atoms. In the models of fig. 1 there is no hydrogen in F and Na, but there are particles of mass $2\frac{1}{3}$ which must behave much like hydrogen if they exist. If they carry a charge of $2e$ when liberated from the atom, the value of e/m would be $2/2\frac{1}{3}$ as compared with that for hydrogen $1/1 \cdot 008$, which would make it more difficult to distinguish them from hydrogen than it would be if they carry but a single charge. It seems important to ascertain experimentally whether or not all these great range particles are hydrogen.

The atoms of magnesium and aluminium may be added to the list above given. There have been reported isotopes of magnesium having masses 24, 25, and 26, the greater number having mass 24. This atom may consist of an inner ring of two alpha-particles and four connecting electrons around which is an outer ring like oxygen consisting of four alpha-particles and eight connecting electrons. The total mass is thus $6\times4=24$, and atomic number $4+8=12$.

The isotopes of 25 and 26 are obtainable by inserting a hydrogen atom into the inner ring as in Gl fig. 1 *b*, and as in Gl–2 fig. 1. These additions do not affect the atomic number, which is 12 for all three isotopes.

Aluminium is based upon the boron atom just described to which the oxygen atom is added. The mass is thus $11{\cdot}024+16=27{\cdot}024$, and the atomic number $5+8=13$ as it should be. The experimental isotopes of Al have not been reported as yet. One and two hydrogen atoms may be added to these rings without affecting the atomic number. Thus the normal Al atom of mass 27·024 is rich in hydrogen, which is not present in magnesium, and the extreme range of 90 cm. for the particles from Al indicates the presence of hydrogen. As in the boron atom the diameter through these hydrogen atoms is a line of weakness because they are neutral atoms, so here this diameter is proportionally weaker. It seems that the bombarding alpha-particles may easily break this ring into two parts along this line of weakness and thus liberate hydrogen with considerable energy in agreement with the observed facts.

Part II.

Computation of the Distances between the Centres o the Atoms forming Molecules.

1. *General Considerations.*

It goes without saying that all of the computations required for the multitudinous combinations known to the chemist of the atoms shown in fig. 1 have not been completed. But the general formulæ to which they are subject have been developed, and their application to these forms will afford a satisfactory test of these ideas. It seems best to have in mind concrete forms with the understanding that the exact positions of the electrons are subject to investigation. Certain combinations have been calculated, and so far as they go the results are in agreement with the known facts.

Since the discovery by Laue of the diffraction patterns produced when X-rays pass through a crystal, the distances between the centres of the atoms in many crystals have been accurately measured. There are not many dimensions in the whole atomic realm in which one has such great confidence as the distances between the centres of the atoms in a crystal. The remarkable thing is that they are all of substantially the same order of magnitude, equal to a small number times 10^{-8} cm. for all known solids and liquids differing widely in atomic weight and number. The greatest known distance between the nearest atoms in any solid is probably within a factor of ten times the least known distance for any other solid. In the case of such elements as aluminium and lead differing greatly in atomic weight, the edge of the elementary cube lattice is about the same—4·07 for Al as compared with 4·91 for Pb.

These distances might conceivably have been many times less than they are, and possibly greater, since the dimensions of the electron above given are of the order of 10^{-13} cm., 100,000 times smaller. The distances between atoms might easily have been 10^{-9}, 10^{-10}, or 10^{-11} cm. unless there is some fundamental cause regulating it that applies to all atoms in common. These considerations lead directly to the thought constituting the theme of this paper, namely, that the general cause contributing to an equilibrium distance in all solids is connected with the properties of the positive and negative electrons themselves common to all atoms. Minor variations in this distance only are brought about by the special configurations of these electrons in the atoms, as in the models.

It is shown in this paper that the non-spherical shape of the negative electron is the principal cause of this particular value, 10^{-8} cm., which is known to be confined within such narrow limits.

Not much is known with the same degree of certainty about the distances between the centres of the atoms in the chemical molecules consisting of but a few atoms, but the presumption is that the order of magnitude is the same as in the crystal molecule, the whole crystal being regarded as one molecule, and that the fundamental cause operating to hold these atoms apart is no different in the one case from the other.

It is still an outstanding question what is the nature of the forces holding atoms at a distance from each other in equilibrium at all, and especially at such uniform distances. Modern atomic theories have postulated many things which depart from electromagnetic theory in their fundamentals in order to obtain some cause for holding two atoms together, as in the diatomic molecule, for example. The Bohr form of theory sets electromagnetic theory aside at the outset in postulating electrons moving in orbits at such speeds that they must lose energy by radiation. The Lewis-Langmuir theory, as extended by Langmuir, does the same thing when it requires an oscillation of an electron back and forth in any form of arc or curve. Without some motion of this kind in the latter theory the system loses stability; their diatomic molecule becomes a system of four point charges in effect with two electrons, say, held in common between the two atoms, and the nucleus of each has a single charge. Such a system of point charges without motion of some kind does not form a stable electrostatic system. All such proposals depart in their fundamental assumptions from any form of electromagnetic theory.

The investigation in this paper assumes in dealing with the atomic models shown in fig. 1 that electromagnetic theory is adhered to, there being no exceptions. In view of these circumstances a thorough search has been made for some possible reason that will satisfactorily account for the known distances between the atoms without at the same time abandoning electromagnetic theory at any point, and without altering the fundamental character of the models.

It cannot be said to be known whether each atom in a crystal or in a molecule is a neutral atom of small dimensions, or whether each has some of its electrons at considerable distance from the atomic centre. The latter alternative is assumed in the Lewis-Langmuir theory, and is perhaps the generally accepted idea of most physicists. The conception introduces insurmountable difficulties in conceiving of the phenomenon by means of electromagnetic theory alone without other postulates that depart from it, and it is shown in this paper that the assumption of neutral atoms, which is in accord with electromagnetic theory, does afford a solution of the matter. This is considered to be sufficient justification for making the assumption of neutral atoms, which is made in the following investigation.

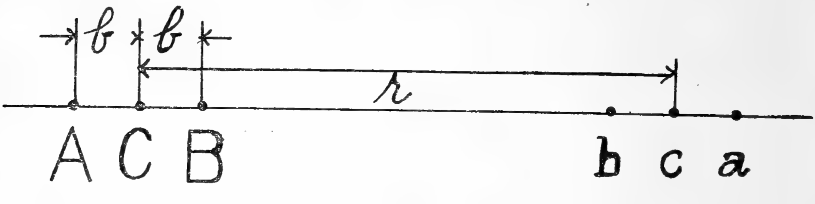


Fig. 4.—Representing the centres of the charges in two hydrogen atoms coaxial with each other. C and *c* are positive charges of $2e$ each, and A, B, *a*, and *b* are the centres of the negative electrons.

If an atom is pictured as composed of some symmetrical arrangement of charges in close proximity to each other, as in fig. 4 for example, that is close compared with the distance to the next atomic centre, then it has been shown that the total electrostatic force between two such atoms follows the inverse sixth power of the distance law, *assuming that each charge is a point charge and obeying the inverse square* *law as regards each other.* The inverse second and fourth power coefficients in the development of the force as a series of powers of r cancel when the atoms are neutral, leaving the principal term of the series the inverse sixth power, which has a negative coefficient meaning a repulsive force between the two neutral groups. Examples of this are given in earlier papers *, but it is again illustrated here by the use of two of the model hydrogen atoms similar to that described.

Let the two atoms be placed at a distance apart, each having a common axis of rotation, as in fig. 4, which shows merely the locations of the centres of the charges, ABC being one atom and abc the other. A and B, also a and b, are negative electrons of charge $-e$, while C and c are positive charges of plus $2e$ each. The rotations of the charges on their axes are to be neglected in this preliminary discussion. Denote the distance Cc by r, and the distances $AC=CB=ac=cb$ by b. The sum of the repulsive forces between the pairs Cc, Ab, and Ba, each at distance r, is according to the inverse square law,

$$F=\frac{e^2}{k}(-6)r^{-2}. \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

There are two other repulsive forces, that of A for a, and of B for b, which give respectively

$$F=\frac{e^2}{k}(-1)(r+2b)^{-2}, \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

and

$$F=\frac{e^2}{k}(-1)(r-2b)^{-2}. \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

There are also four attractive pairs which partly balance the above, that of A for c and of C for a at a distance $r+b$, and that of C for b and of B for c at distance $r-b$, which give respectively when added

$$F=\frac{e^2}{k}(4)(r+b)^{-2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

and

$$F=\frac{e^2}{k}(4)(r-b)^{-2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

The expansion of these quantities in series gives

$$(r+2b)^{-2}+(r-2b)^{-2}=2r^{-2}+24b^2r^{-4}+160b^4r^{-6}\ldots, \qquad (6)$$

$$(r+b)^{-2}+(r-b)^{-2}=2r^{-2}+6b^2r^{-4}+10b^4r^{-6}\ldots. \qquad (7)$$

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* Phil. Mag. July 1913, pp. 39, 66, 71; and June 1915, pp. 755, 764.

Hence the sum of (1) to (5) inclusive gives the whole electrostatic force between these two groups of charges, namely

$$F = \frac{e^2}{k}(-120)b^4r^{-6} \dots \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This is still a very large repulsive force, and attempts were made in former papers to balance this against the force due to the revolutions of the electrons in orbits. With the present model, however, we are deprived even of this possibility because the electrons cannot revolve in an orbit completely around the centre of the atom according to electromagnetic theory. To estimate the magnitude of this force, let b be made as small as possible and take $r = 10^{-8}$ cm. The smallest value of b admissible is the minor radius of the electron, say 10^{-13} cm., so that

$$F = \frac{e^2}{k}(-0{\cdot}012) \text{ dynes.} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This is equal to the repulsion between two electrons at a distance of about 9 cm. No forces are available due to the rotation of the electrons on their axes to balance this great force. For some time this difficulty has been a stumbling block to further progress.

It was not until the idea was used that the negative electrons and the positive charge, as discussed in the preceding paper, do not have a spherical shape that it was perceived the electrostatic force just calculated must be revised, because the assumed form of an oblate spheroid cannot be treated as a sphere for external points. Let us, therefore, recompute the electrostatic force for the combination of charges represented in fig. 4, the hydrogen molecule.

To undertake this brings us at once into unexplored territory, for the solution depends in part upon the electrostatic force between two solid oblate spheroids of charge—a problem that has not been solved in its generality. We shall, therefore, limit ourselves in this preliminary investigation to the case of two spheroids having a common axis of revolution, and besides this approximate the spheroid by dividing it into two parts—first the sphere inscribed within it, and second the rest of the spheroid. Let the charge of the inscribed sphere be denoted by E_1 and of the rest by E_2, so that

$$E_1 + E_2 = e \text{ for the negative electron.} \quad . \quad . \quad . \quad (10)$$

The reason for making this division is because the sphere may be treated as a point charge for all external points, and the rest of the spheroid approximates a ring or circle of a certain unknown radius, say a, and may be treated as a single ring uniformly charged, the solution for which is known. In view of the uncertainty as to the precise shape of the electron, this substitution of a ring and a point as the equivalent of the negative electron electrostatically may be just as appropriate as to use the solution for the spheroid were it known.

2. *The Electrostatic Force of One Non-spherical Electron upon Another Coaxial with it.*

Represent the meridian section of the two coaxial electrons as in fig. 5 by ellipses of semi-major axis a_0 and semi-minor axis b, and imagine the inscribed sphere to be replaced by a point of charge E_1 and the rest by a ring of unknown radius, a. The fundamental problem is to find the electrostatic force between two coaxial rings of different radii. Although the radii of the rings for the two electrons are equal, yet to find the force between a ring and a point it is convenient to use the same expression and equate one of the radii to zero for the point.

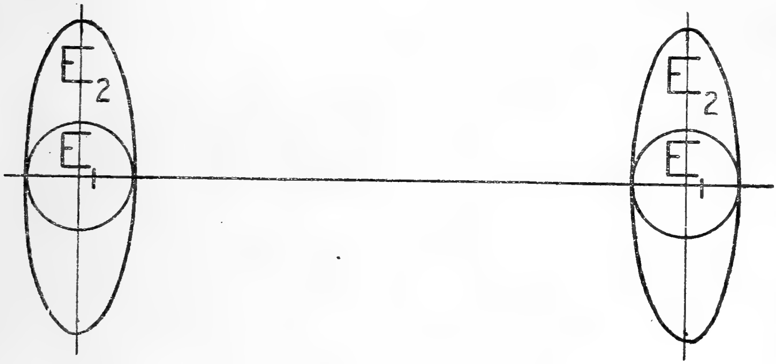

Fig. 5.—Representing the meridian section of two coaxial electrons, the charge in the inscribed sphere being electrostatically equivalent to a point, and of the rest equivalent to a ring.

The complete general expression for the average electrostatic force resolved along the centre line, r, between two point charges in circles of different radii but having parallel axes is given by equation (42) of a former paper *. In the special case

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* Phil. Mag. July 1913, eq. (42).

of coaxial circles the angle of latitude, λ, which occurs in the formula becomes $\pi/2$, and $\cos\lambda=\Lambda=0$. With this simplification most of the terms in this equation drop out, leaving in the notation there employed the r-component of the force of one element of one ring upon one element of the other:

$$F_r=-\frac{dE_1dE_2\Delta^3v}{ka_*^2}\{A_{0,0}+A_{2,0}\delta\Gamma\Delta^2+A_{4,0}\delta^2\Gamma^2\Delta^4$$
$$+A_{6,0}\delta^3\Gamma^3\Delta^6+A_{8,0}\delta^4\Gamma^4\Delta^8\ldots\},\quad(11)$$

where the numerical coefficients follow the scheme

$$A_{0,0}=1\ ;\quad A_{2,0}=3A_{0,0}=3\ ;\quad A_{4,0}=\tfrac{5}{2}A_{2,0}=15/2\ ;$$
$$A_{6,0}=\tfrac{7}{3}A_{4,0}=35/2\ ;\quad A_{8,0}=\tfrac{9}{4}A_{6,0}=315/8\ ;\quad \text{etc.}\ ;$$

and the symbols are abbreviations for the following. The distance between the centres of the circles is r when measured in centimetres, and is v when measured in a small unit a_*, so that $r=a_*v$. The radii of the orbits are a_1 and a_2, or a_*m and a_*n, so that $a_1=a_*m$ and $a_2=a_*n$. $\delta=mn$, and $\Delta=(v^2+m^2+n^2)^{-1/2}$. $\Gamma=\cos\gamma$, where γ is the phase difference between the two elements of charge. k is the dielectric constant.

The first process is to integrate for the phase angle, γ, around one circle between the limits of 0 and 2π, which may be accomplished by replacing all odd powers of the cosine by zero and the even powers by $\cos^2\gamma=1/2$, $\cos^4\gamma=3/8$, &c., as in averaging. These substitutions enable us to derive from (11) the total force between coaxial circles,

$$F_r=\frac{-E_1E_2\Delta^3v}{ka_*^2}\left\{1+\frac{15}{4}m^2n^2\Delta^4+\frac{945}{64}m^4n^4\Delta^8+\ldots\right\}.\quad(12)$$

The expansions of Δ^3v, &c. in series give the following, where $M=m^2+n^2$:

$$\Delta^3v=v^{-2}-\frac{3}{2}Mv^{-4}+\frac{15}{8}M^2v^{-6}-\frac{35}{16}M^3v^{-8}$$
$$+\frac{315}{128}M^4v^{-10}\ldots$$

$$\frac{15}{4}m^2n^2\Delta^7v=\qquad+\frac{15}{4}m^2n^2v^{-6}-\frac{105}{8}Mm^2n^2v^{-8}$$
$$+\frac{945}{32}M^2m^2n^2v^{-10}\ldots$$

$$\frac{945}{64}m^4n^4\Delta^{11}v=\qquad+\frac{945}{64}m^4n^4v^{-10}\ldots\ ;$$

so that, when r, a_1, and a_2 are restored, the whole electrostatic force upon one ring due to a second coaxial with it becomes

$$\underset{\substack{\text{ring}\\ \text{on ring.}}}{F_r} = \frac{E_1E_2}{k}\Big\{ -r^{-2} + \frac{3}{2}(a_1^2+a_2^2)r^{-4} - \left[\frac{15}{8}(a_1^2+a_2^2)^2 + \frac{15}{4}a_1^2a_2^2\right]r^{-6}$$
$$+\left[\frac{35}{16}(a_1^2+a_2^2)^3 + \frac{105}{8}(a_1^2+a_2^2)a_1^2a_2^2\right]r^{-8}$$
$$-\left[\frac{315}{128}(a_1^2+a_2^2)^4 + \frac{945}{32}(a_1^2+a_2^2)^2a_1^2a_2^2 + \frac{945}{64}a_1^4a_2^4\right]r^{-10}\dots\Big\}. \quad \dots \quad (13)$$

By making the radii both equal to a and the charges both equal to E_2 we have the force between two rings of the same radius and charge:

$$\underset{\substack{\text{ring}\\ \text{on ring.}}}{F_r} = \frac{E_2^2}{k}\left\{ -r^{-2} + 3a^2r^{-4} - \frac{45}{4}a^4r^{-6} + \frac{175}{4}a^6r^{-8} - \frac{11025}{2^6}a^8r^{-10}\dots\right\}. \quad \dots \quad (14)$$

To check this result, the force (14) may be directly derived from the expression for the force between two elements of the two rings, namely

$$dF = \frac{-dE_1dE_2}{k}\frac{r}{[r^2+2a^2(1-\cos\gamma)]^{3/2}}. \quad \dots \quad (15)$$

By expanding the denominator in series and integrating each term separately for the phase angle γ between the limits 0 and 2π, it has been shown that equation (14) results. The general equation used above, however, will be of much use in other cases.

By making $a_1=0$ and $a_2=a$ we obtain from (13) the force of a ring of charge, E_2, upon a point of charge E_1, namely

$$\underset{\substack{\text{ring}\\ \text{on point.}}}{F_r} = \frac{E_1E_2}{k}\left\{ -r^{-2} + \frac{3}{2}a^2r^{-4} - \frac{15}{8}a^4r^{-6} + \frac{35}{16}a^6r^{-8} - \frac{315}{128}a^8r^{-10}\dots\right\}. (16)$$

To find from these the whole electrostatic force of one non-spherical electron upon the other, as in fig. 5, add to (14) twice (16) and include the force of E_1 in one electron on E_1 in the other as point charges, giving

$$\underset{\substack{\text{electron}\\ \text{on electron.}}}{F_r} = \frac{1}{k}\Big\{ -e^2r^{-2} + 3E_2(E_2+E_1)a^2r^{-4}$$
$$-\frac{15}{4}E_2(3E_2+E_1)a^4r^{-6} + \frac{35}{8}E_2(10E_2+E_1)a^6r^{-8}$$
$$-\frac{315}{64}E_2(35E_2+E_1)a^8r^{-10}\dots\Big\}. \quad \dots \quad (17)$$

It will be convenient to define the ratio E_2/e by the unknown quantity, ρ, so that e^2 may be factored out from (17), giving

$$\underset{\substack{\text{electron}\\\text{on electron.}}}{F_r} = \frac{e^2}{k}\Big\{-r^{-2}+3\rho a^2r^{-4}-\frac{15}{4}\rho(2\rho+1)a^4r^{-6}$$
$$+\frac{35}{8}\rho(9\rho+1)a^6r^{-8}-\frac{315}{64}\rho(34\rho+1)a^8r^{-10}\ldots\Big\}. \quad . \quad . \quad . \quad (18)$$

This equation forms the basis for computing the electrostatic force between two coaxial groups of charges, the two atoms of fig. 4. It is to be noted that the force between two electrons does not now follow the inverse square law, but that the forces between elements of their charges do.

3. *The Electrostatic Force upon one* H-*atom due to another Coaxial* H-*atom according to the Atomic Model.*

Using (18) as the force between two coaxial electrons instead of considering them to be point charges as in the previous example, it may stand without change as representing the force of the electron A on b, or of B on a in fig. 4, since each distance is equal to r. To find the force between the most distant pair of electrons, A on a, the distance r must be changed to $r+2b$. Expanding $(r+2b)^{-2}$, $(r+2b)^{-4}$, etc. and multiplying by the coefficients in (18) gives

$$\underset{\text{A on }a.}{F} = \frac{e^2}{k}\{Ar^{-2}+Br^{-3}+Cr^{-4}+Dr^{-5}+Er^{-6}+Fr^{-7}$$
$$+Gr^{-8}+Hr^{-9}+Ir^{-10}\ldots\},$$

where

$$A=-1\,;\quad B=4b\,;\quad C=-12b^2+3\rho a^2\,;\quad D=(32b^2-24\rho a^2)b\,;$$
$$E=-80b^4+120\rho a^2b^2-\frac{15}{4}\rho(2\rho+1)a^4\,;$$
$$F=192b^5-480\rho a^2b^3+45\rho(2\rho+1)a^4b\,;$$
$$G=-448b^6+1680\rho a^2b^4-315\rho(2\rho+1)a^4b+\frac{35}{8}\rho(9\rho+1)a^6\,;$$
$$H=1024b^7-5376\rho a^2b^5+1680\rho(2\rho+1)a^4b^3-70\rho(9\rho+1)a^6b\,;$$
$$I=-2304b^8+16128\rho a^2b^6-7560\rho(2\rho+1)a^4b^4$$
$$+630\rho(9\rho+1)a^6b^2-\frac{315}{64}\rho(34\rho+1)a^8. \quad . \quad (19)$$

The force between the inside pair of electrons, B on b, is the same as (19) in all the even powers of r, while the signs of the odd powers are reversed. The attractive forces are those between the positive charges and the electrons. Equation (16) gives the force between a ring and a point charge, and the positive charge may still be regarded as a point because of its very small dimensions, 10^{-16} cm., as compared with that of the electron, 10^{-13} cm. By changing E_1 in (16) to positive $2e$, which changes the sign of the expression, we have the force between the ring of the electron and the positive charge. To this must be added the force of E_1, the inscribed sphere, upon the positive charge, each being a point charge, giving at the distance r:

$$\underset{\substack{\text{electron}\\ \text{on } 2e.}}{\mathrm{F}} = \frac{e^2}{k}\left\{2r^{-2} - 3\rho a^2 r^{-4} + \frac{15}{4}\rho a^4 r^{-6} - \frac{35}{8}\rho a^6 r^{-8} + \frac{315}{64}\rho a^8 r^{-10}\ldots\right\}. \quad . \quad . \qquad (20)$$

To obtain from this the force of the most distant electron a on the positive charge C, change r in (20) into $r+b$, giving

$$\underset{\substack{a \text{ on C}\\ \text{or C on } a.}}{\mathrm{F}} = \frac{e^2}{k}\{\mathrm{A}r^{-2} + \mathrm{B}r^{-3} + \mathrm{C}r^{-4} + \mathrm{D}r^{-5} + \mathrm{E}r^{-6} + \mathrm{F}r^{-7} + \mathrm{G}r^{-8} + \mathrm{H}r^{-9} + \mathrm{I}r^{-10} + \ldots\},$$

where

$$\mathrm{A}=2\,; \quad \mathrm{B}=-4b\,; \quad \mathrm{C}=6b^2-3\rho a^2\,; \quad \mathrm{D}=-8b^3+12\rho a^2 b\,;$$

$$\mathrm{E}=10b^4-30\rho a^2b^2+\frac{15}{4}\rho a^4\,; \quad \mathrm{F}=-12b^5+60\rho a^2b^3-\frac{45}{2}\rho a^4 b\,;$$

$$\mathrm{G}=14b^6-105\rho a^2b^4+\frac{315}{4}\rho a^4b^2-\frac{35}{8}\rho a^6\,;$$

$$\mathrm{H}=-16b^7+168\rho a^2b^5-210\rho a^4b^3+35\rho a^6 b\,;$$

$$\mathrm{I}=18b^8-252\rho a^2b^6+\frac{945}{2}\rho a^4b^4-\frac{315}{2}\rho a^6b^2+\frac{315}{64}\rho a^8. \quad . \qquad (21)$$

The force of the nearer electron, b, upon the positive charge is the same as (21) except that the signs of the odd powers of r are reversed. Hence the electrostatic force of the whole atom (ABC) upon the distant electron, a, of the other atom is the sum of A on a (19), B on a (18), and C on a (21), giving

$$\underset{\substack{\text{atom ABC}\\ \text{on } a.}}{\mathrm{F}} = \frac{e^2}{k}\{\mathrm{A}'r^{-4} + \mathrm{B}'r^{-5} + \mathrm{C}'r^{-6} + \mathrm{D}'r^{-7} + \mathrm{E}'r^{-8} + \mathrm{F}'r^{-9} + \mathrm{G}'r^{-10}\ldots\},$$

where

$$A' = 3(\rho a^2 - 2b^2)\,; \qquad B' = -12b(\rho a^2 - 2b^2)\,;$$

$$C' = -70b^4 + 90\rho a^2 b^2 - \frac{15}{4}\rho a^4 - 15\rho^2 a^4\,;$$

$$D' = b\left(180b^4 - 420\rho a^2 b^2 + \frac{45}{2}\rho a^4 + 90\rho^2 a^4\right);$$

$$E' = -434b^6 + 1575\rho a^2 b^4 - \frac{945}{4}\rho a_4 b^2 + \frac{35}{8}\rho a^6$$
$$-630\rho^2 a^4 b^2 + \frac{315}{4}\rho^2 a^6\,;$$

$$F' = 1008b^7 - 5208\rho a^2 b^5 + 3360\rho^2 a^4 b^3 + 1470\rho a^4 b^3$$
$$-630\rho^2 a^6 b - 35\rho a^6 b\,;$$

$$G' = -2286b^8 + 15876\rho a^2 b^6 - \frac{14175}{2}\rho a^4 b^4 + \frac{945}{2}\rho a^6 b^2$$
$$-\frac{315}{64}\rho a^8 - 15120\rho^2 a^4 b^4 + 5670\rho^2 a^6 b^2 - \frac{5355}{16}\rho^2 a^8. \quad \ldots\ldots \quad (22)$$

The electrostatic force of the whole atom ABC upon the near electron b is the same as (22) with the signs of the odd powers of r reversed. The electrostatic force of the whole atom ABC upon the positive charge of the other is given by (21), for a on C or A on c, added to (21) with signs of odd powers reversed for B on c, and added to $-4e^2/kr^2$ for the force of C on c, giving

$$\underset{\substack{\text{atom ABC}\\ \text{on } c.}}{F} = \frac{2e^2}{k}\{Cr^{-4} + Er^{-6} + Gr^{-8} + Ir^{-10}\ldots\}, \quad . \quad (23)$$

where the coefficients have the same values as in (21).

Similarly, the force of the atom ABC upon the two electrons of the other atom is found by adding to (22) the same equation (22) with odd powers reversed, giving

$$\underset{\substack{\text{atom ABC}\\ \text{on } (a+b).}}{F} = \frac{2e^2}{k}\{A'r^{-4} + C'r^{-6} + E'r^{-8} + G'r^{-10}\ldots\}, \quad (24)$$

where the coefficients are the same as in (22).

The whole electrostatic force of the atom ABC upon *abc* is, therefore, the sum of (23) and (24), namely

$$\underset{\substack{\text{atom ABC}\\ \text{on atom } abc.}}{F} = \frac{2e^2}{k}\{(C + A')r^{-4} + (E + C')r^{-6} + (G + E')r^{-8}$$
$$+ (I + G')r^{-10}\ldots\},$$

where

$$C+A'=0,$$

$$E+C'=-60b^4+60\rho a^2b^2-15\rho^2a^4=-15(2b^2-\rho a^2)^2,$$

$$G+E'=-420b^6+1470\rho a^2b^4-\frac{315}{2}\rho a^4b^2-630\rho^2a^4b^2+\frac{315}{4}\rho^2a^6,$$

$$\begin{aligned}I+G'=-2268b^8+15624\rho a^2b^6-6615\rho a^4b^4+315\rho a^6b^2\\ -15120\rho^2a^4b^4+5670\rho^2a^6b^2-\frac{5355}{16}\rho^2a^8.\end{aligned} \qquad (25)$$

The coefficient of the r^{-4} term, therefore, vanishes for the non-spherical electrons just as it did in the preceding example for the case of point charges. In the former example the r^{-6} term gave a strong repulsion for the electrostatic force between the two atoms, but now the r^{-6} coefficient, $E+C'$, depends upon the relative values of b and a, that is, depends entirely upon the shape of the electron. It was pointed out above that the large coefficient of the r^{-6} term in the point-charge example prevented further progress, because there cannot possibly be a force due to the motion of charges great enough to neutralize this repulsion and give an equilibrium distance. In order that the r^{-6} term of (25) shall vanish it must be true that

$$2b^2=\rho a^2 \quad \text{or} \quad \frac{a}{b}=\left(\frac{2}{\rho}\right)^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (26)$$

Let us examine this relation in some detail because it reveals the limits between which the eccentricity of the ellipse representing the meridian section of the electron lies. It may be shown that ρ is equal to the square of the eccentricity of the ellipse, for by definition $\rho=E_2/e$, and on account of the assumption of uniform density the two charges E_2 and e are proportional to their volumes. Hence we have

$$\frac{\text{Vol. ellipsoid}}{\text{Vol. inscribed sphere}}=\frac{\frac{4}{3}\pi a_0{}^2b}{\frac{4}{3}\pi b^3}=\frac{a_0{}^2}{b^2}=\frac{e}{E_1}=\frac{e}{e-E_2}=\frac{1}{1-\rho}, \quad . \quad . \quad . \quad (27)$$

whence

$$\rho=\frac{a_0{}^2-b^2}{a_0{}^2}=\epsilon^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

the square of the eccentricity. Hence the relation to be studied (26) becomes

$$a/b=\sqrt{2}/\epsilon. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

This ratio, the unknown radius of the equivalent ring of the electron to the semi-minor axis, is plotted in Curve I. fig. 6, as ordinates against the eccentricity, ϵ, as abscissæ by the use of (29). From the geometrical properties of the ellipse the ratio of the semi-major to the semi-minor axis in terms of the eccentricity is

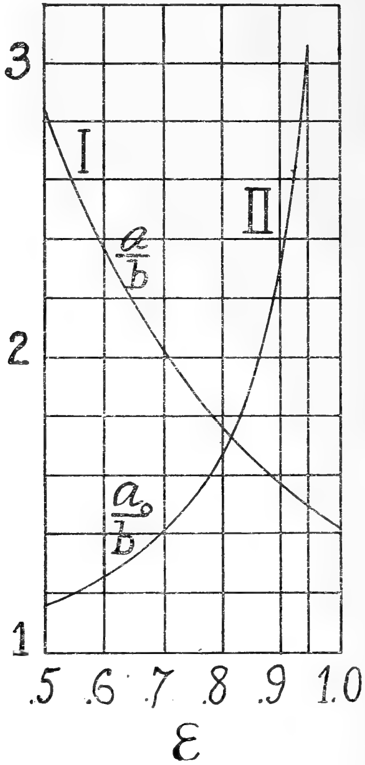

Fig. 6.—Curve I. is the graph of the ratio of the radius of the ring of the equivalent electron to the semi-minor axis obtained from (29). $a/b=\sqrt{2}/\epsilon$. Curve II. is the graph of the ratio of the semi-major to the semi-minor axis of the electron, both ratios being plotted against the eccentricity. The curves show that the eccentricity must be greater than $\epsilon=\cdot 82$ the point of intersection, and they indicate that the eccentricity must exceed about ·9. The valu used is ·945, corresponding to $a_0/b=3{\cdot}058$.

$$a_0/b = (1-\epsilon^2)^{-1/2},$$

which is plotted as Curve II. fig. 6. The two curves intersect at an eccentricity about ·82. For all eccentricities less than this the unknown radius, a, would have to be greater than the semi-major axis of the ellipse, when the equivalent ring would lie wholly outside of the ellipsoid, a result that is physically absurd. The eccentricity must certainly be greater than ·82 in order to satisfy (26) and reduce the r^{-6} coefficient to zero, and must lie between ·82 and unity as an upper limit. At an eccentricity ·9 it is seen that $a/b=1{\cdot}57$, $a_0/b=2{\cdot}3$, and $a/a_0={\cdot}68$. A rough estimation of the position of the equivalent radius would indicate that ·9 is certainly a lower limit for the eccentricity. There is no obvious way to compute the radius a from electrostatic forces alone.

It seems, therefore, remarkable that the eccentricity of the electron as determined in the first paper * by an entirely different method should have yielded a value within the limits above found, namely $\epsilon={\cdot}945$, corresponding to ratios $a/b=1{\cdot}5$, $a/a_0={\cdot}5$ approximately, and $a_0/b=3{\cdot}058$, shown in fig. 6 by the ordinate at ·945. These two independent determinations taken together not only help to establish the non-spherical form of the electron, but they approximately determine its value within fairly narrow limits.

Let us now proceed with the assumption that (29) is exactly satisfied by the properties of the electron, and examine the values that the various coefficients assume by introducing this relation. From (26) we have

$$\begin{aligned} \rho a^2 &= 2b^2, & \rho^2 a^4 &= 4b^4, \\ \rho a^4 &= 4b^4/\rho, & \rho^2 a^6 &= 8b^6/\rho, \\ \rho a^6 &= 8b^6/\rho^2, & \rho^2 a^8 &= 16b^8/\rho^2, \\ \rho a^8 &= 16b^8/\rho^3, & & \quad . \quad . \quad . \quad (30) \end{aligned}$$

and these values reduce both (E+C′) and (G+E′) in (25) to zero identically. That is to say, both the r^{-6} and the r^{-8} terms of the series disappear together, while the coefficient of the r^{-10} term, (I+G′), becomes

$$(-31500+18900/\rho-2835/\rho^2)b^8. \quad . \quad . \quad . \quad (31)$$

Using the value of the eccentricity as first determined, namely ·945, ρ is given by (28), and $1/\rho$ is 1·12 approximately. Hence the whole electrostatic force between the two atoms given by (25) becomes numerically

$$\underset{\substack{\text{atom ABC}\\ \text{on atom } abc.}}{\mathrm{F}} = \frac{e^2}{k}(-27776b^8r^{-10}\ldots), \quad . \quad . \quad . \quad (32)$$

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* Phil. Mag. Oct. 1921, equation (76).

That this series is so rapidly convergent at distances comparable with 10^{-8} cm. that the first term of it represents very approximately the whole force may be shown as follows. The approximate value of b/r is $10^{-13}/10^{-8}=10^{-5}$, so that $b^8/r^8=10^{-40}$, $b^{10}/r^{10}=10^{-50}$, etc., and so that $b^8r^{-10}=10^{-24}$, $b^{10}r^{-12}=10^{-34}$, etc., these values decreasing in the ratio of 10^{10}. In all succeeding terms the exponent of b is always two less than the exponent of r but with opposite sign. The numerical coefficients do not increase at any such rate as 10^{10}, and the r^{-12} and succeeding terms are of no value. The *electrostatic* force between these atoms therefore varies as the inverse tenth power of the distance between their centres, when (26) is satisfied.

In a similar manner the condition that (26) is satisfied reduces the force of the atom ABC on the positive charge c (23) to

$$\underset{\substack{\text{atom ABC}\\ \text{on } c.}}{\mathrm{F}}=\frac{2e^2}{k}\{-5(10-3/\rho)b^4r^{-6}+(-196+315/\rho-35/\rho^2)b^6r^{-8}$$
$$+(-486+1890/\rho-1260/\rho^2$$
$$+1260/\rho^3)b\,r^{-10}\ldots\}, \quad . \quad . \quad . \quad . \quad (33)$$

and reduces the force upon the two electrons $(a+b)$ due to ABC in (24) to

$$\underset{\substack{\text{atom ABC}\\ \text{on } (a+b).}}{\mathrm{F}}=\frac{2e^2}{k}\{5(10-3/\rho)b^4r^{-6}+(196-315/\rho+35/\rho^2)b^6r^{-8}$$
$$+(-31014+17010/\rho-1575/\rho^2$$
$$-1260/\rho^3)b^8r^{-10}\ldots\}. \quad . \quad . \quad . \quad . \quad (34)$$

These two equations are exactly equal but of opposite sign in both the r^{-6} and r^{-8} terms, and, since the first term represents practically the whole of the force, it may be said that the force upon the nucleus is one of repulsion equal to the first term of (33), while that upon each electron is an attraction equal to one half the first term of (34) electrostatically. These forces are very large, varying as the inverse sixth power in comparison with their sum which varies as the inverse tenth power. It is this smaller force which must be balanced by terms due to the rotation of the positive nuclei, which will now be considered.

Terms due to Rotation.

Fortunately the solution for the mutual action of two continuous rings of charge in rotation has been solved in its generality, using the Saha equation so far as the inverse square of the distance terms are concerned. At distances comparable with 10^{-8} cm. the ratio of the distances, 10^{-8} cm., to the dimensions of the atoms shown in fig. 1, varies between 30000 and 8000 approximately, being so great that the second atom may still be considered to be at a great distance from the first. It may be shown that the higher order terms than the second are negligible, and that the whole force due to the rotation of the charges is merely that given by the gravitational law, modified where single atoms are considered by terms defining the directions of their axes. This result is given in the general form in equation (57) of the first paper*, and in (59) when the force is resolved along the centre line joining the rings. Summing up the Z-component force for the axis case, where Z=1 and X=0, by means of the equation referred to for the whole hydrogen atom acting upon another hydrogen atom, we find

$$F = \frac{e^2}{k}(2\beta_2^4 r^{-2}). \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Adding this to the electrostatic force found above in (32) gives the complete force upon the first atom due to the second as

$$F = \frac{e^2}{k}(2\beta_2^4 r^{-2} - 27776 \,.\, b^8 r^{-10}), \quad . \quad . \quad . \quad (36)$$

whence equating to zero for equilibrium, and solving for r, we have †

$$r^8 = 13888 \cdot \frac{b^8}{\beta_2^4} \quad \text{and} \quad r = 1{\cdot}18 \times 10^{-8} \text{ cm.} \quad . \quad (37)$$

This represents the distance between the two atoms of the diatomic hydrogen molecule. It may be seen that the equilibrium is stable in the direction of the axis, for an increase of the distance r makes the gravitational r^{-2} term in excess of the other term, meaning that the atoms are attracted, while a decrease of the distance makes the repulsive force in excess

As to stability the other way perpendicular to the axis, this matter must be referred to the X-component of the force which has not been developed above. It may be stated, however, that the general form of equation has been developed, and is discussed in detail in the next paper III.

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* *Loc. cit.*

† The numerical values of b and β_2 used here are the same as previously found in the first paper, $b=1{\cdot}065\times10^{-13}$ and $\beta_2^4=0{\cdot}6053\times10^{-36}$.

Helium.

Fig. 7 may represent two helium atoms similar to that of fig. 1, lined up so as to have a common axis of rotation.

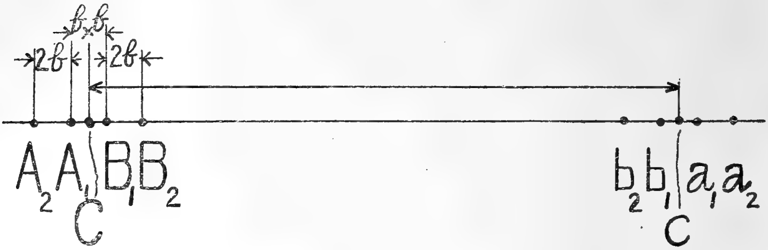

Fig. 7.—Representing the centres of the charges in two helium atoms coaxial with each other.

The positive charge of $4e$ is at C, the four electrons being A_1, A_2, B_1, and B_2. Using the method shown in detail above for hydrogen, the electrostatic force of the atom $(A_2A_1CB_1B_2)$ upon the positive charge of the other atom, c, is

$$\underset{\substack{\text{He-atom}\\ \text{on } c.}}{\mathrm{F}} = \frac{e^2}{k}\{(240b^2-24\rho a^2)r^{-4}+(3280b^4-1200\rho a^2b^2 +30\rho a^4)r^{-6}\ldots\}. \quad . \quad . \quad (38)$$

The electrostatic force of the same atom upon the four electrons together $(a_2a_1b_1b_2)$ is

$$\underset{\substack{\text{He-atom}\\ \text{on four electrons.}}}{\mathrm{F}} = \frac{e^2}{k}\{(-240b^2+12\rho a^2)r^{-4}+(-15280b^4+3600\rho a^2b^2 -90\rho^2a^4-15\rho a^4)r^{-6}\ldots\}. \quad . \quad . \quad (39)$$

The sum of these gives the whole electrostatic force of the second He-atom on the first:

$$\underset{\substack{\text{He-atom}\\ \text{on He-atom.}}}{\mathrm{F}} = \frac{e^2}{k}\{-12\rho a^2r^{-4}+(-12000b^4+2400\rho a^2b^2-90\rho^2a^4 +15\rho a^4)r^{-6}\ldots\}. \quad . \quad (40)$$

Using the relation $2b=\rho a^2$ as before, (40) becomes

$$\underset{\substack{\text{He-atom}\\ \text{on He-atom.}}}{\mathrm{F}} = \frac{e^2}{k}\{-24b^2r^{-4}-(7650-60/\rho)b^4r^{-6}\ldots\}, \quad (41)$$

In the above example with hydrogen all the electrostatic terms vanished up to the r^{-10} term after introducing the relation (26), but here even the r^{-4} term does not vanish and becomes the largest term, showing great repulsion between the atoms. No terms in the inverse square due to the rotation of charges can possibly balance this great repulsion. These repulsive terms will persist in other positions of the atoms aside from the particular axis case considered, and it may be concluded that helium must be monatomic if it is as shown in fig. 1.

The combination of hydrogen with helium on the axis gives as a final result for the electrostatic force:

$$\underset{\substack{\text{He on H}\\ \text{electrostatic.}}}{\mathrm{F}} = \frac{e^2}{k}\{-12b^2r^{-4}+30(2+1/\rho)b^4r^{-6}\ldots\}, \qquad . \quad (42)$$

and here again the r^{-4} repulsive force appears, which prevents helium from uniting with hydrogen. In a similar manner it may, I believe, be shown generally that helium will not unite with any of the other atoms shown in fig. 1. The same statement may be made for neon, which has a helium atom at its centre. The presence of this is sufficient to cause a great repulsive force between the atoms of neon and any other of the atoms shown.

Summary.

In Part I. is presented a concrete picture of the forms of the atoms of the lighter elements including isotopes from hydrogen to sodium inclusive, which are in conformity with the Saha form of electromagnetic theory. The shape adopted for the negative electron is an oblate spheroid with ratio of axes about three to one, as determined in the first paper. Although Rutherford's experimental results were unknown to the writer at the time the models were made, the distance between the centre of the nitrogen atom and the hydrogen in nitrogen is just two diameters of the electron, as he has found.

General formulæ not given in this paper have been developed for testing these atomic forms by determining how they satisfy the known results of chemistry in combining with each other to form molecules.

In Part II. it is shown that the shape of the negative electron is a most important factor in determining the equilibrium distance between two atoms forming a molecule. The approximately constant distance between the centres of atoms in all solids is directly connected with the shape of the electron, and for this reason it is a universal distance. In order that these atoms may unite with each other at all, it is shown that the eccentricity of the electron must lie between

the limits of about ·9 and 1·0. This agrees in a rather remarkable way with the determination of the eccentricity as ·945 in the first paper, which was based on an entirely different assumption.

It has been shown that the helium and neon atoms of fig. 1 will not form compounds with any of the other atoms shown, and that they must be monatomic. The exact determination of some of the simpler molecules is deferred for a future communication on account of space.

XCVIII. *The Disappearance of Gas in the Electric Discharge.*—IV. *By* The Research Staff of the General Electric Company Ltd., London [*]. (*Work conducted by* N. R. CAMPBELL *and* H. WARD.)

THE experiments described in this paper are a continuation of those described in the previous papers of the series [†].

They are concerned primarily with the disappearance of gas in the presence of phosphorus vapour, but some of the conclusions reached are applicable, even when phosphorus is not present.

Summary.

The main experiments are directed to determine how the quantity of gas absorbed in the discharge in the presence of phosphorus varies with various factors.

The experimental methods are described in pars. 3 and 4. The following conclusions are reached concerning the factors :—

1. *The nature of the gas.*—Compound gases and some elements are excluded on the ground of chemical change. Of the rest, the inactive gases are little absorbed ; hydrogen and nitrogen, on which the experiments have been conducted, behave almost identically. (Par. 2.)

2. *The nature of the discharge* has little direct effect upon the amount of gas absorbed. (Par. 5.)

3. *The form of the vessel* is important only in so far as it affects the area of the walls exposed to the discharge. The temperature in the neighbourhood of 20° C. has no effect. (Par. 5.)

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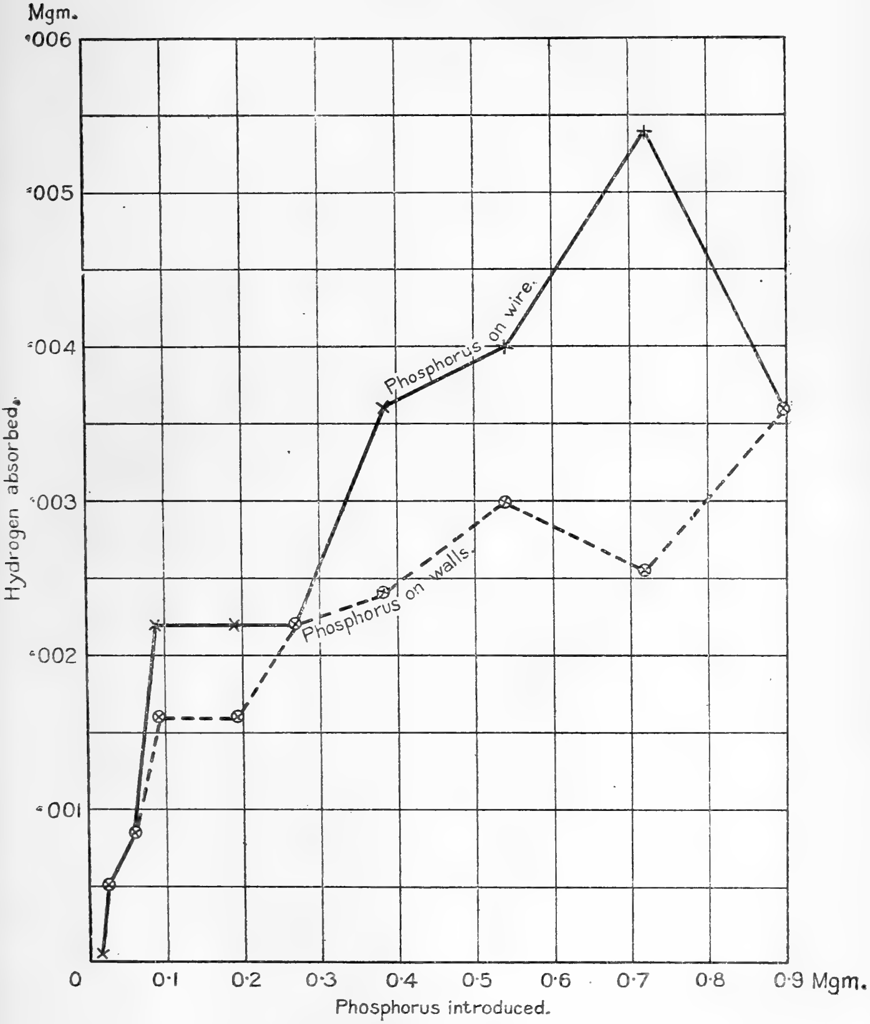
[*] Communicated by the Director.

[†] Research Staff of the G. E. C., London, Phil. Mag. xl. p. 585 (1920); xli. p. 685 (1921); xlii. p. 227 (1921). These papers will be quoted respectively as I., II., III.

4. *The pressure of the gas* during absorption has no effect within wide limits on the amount absorbed. (Par. 6.)

5. The relation between the amount of gas absorbed and the amount of phosphorus present is shown in fig. 1. It is given by a stepped line rather than by a smooth curve. It varies somewhat according to the state in which the phosphorus is introduced. (Par. 7.)

Fig. 1.



6. The state of the walls has no effect within wide limits. All kinds of glass, cleaned or etched by any method or coated with other substances by evaporation of solutions or by chemical action, have the same absorptive power. On the other hand, the absorptive power can be greatly increased by "evaporating" certain substances from an electrically heated filament and so depositing them on the walls. The ionization of the vapour is an important factor in this process. Metallic tungsten is among the substances having this property, but no relation has been found generally between this property and others. These substances act to some extent as substitutes for phosphorus. (Pars. 8–11.)

The following subsidiary matters are dealt with :—

7. In the absence of phosphorus or its substitutes, the absorption is indeterminate, representing a balance between true absorption and liberation. (Par. 12.)

8. The absorption of gas mixed with phosphorus vapour takes place in two stages—a very rapid absorption accompanying the deposition of the phosphorus on the walls, and a slower absorption after it has been deposited. The same two stages are characteristic of the substitutes considered in (6). (Par. 13.)

9. The occurrence of absorption seems determined simply by ionization, and will occur, though very slowly, in the absence of a visible glow. There appears to be no lower limit to the pressure that can be attained by absorption in the presence of phosphorus. (Par. 14.)

10. The gas absorbed is liberated when the phosphorus is evaporated from the walls ; that absorbed under the influence of the substitutes of (6) cannot be liberated because the substitutes cannot be evaporated. There is evidence of the formation of such chemical compounds as PH_3, but none of the formation of compounds which are not formed in other circumstances. The formation of these compounds is a secondary and not a primary feature of the absorption. (Par. 15.)

11. Arsenic appears to have exactly the same properties as phosphorus, as Whitney has found. Sulphur and iodine were not examined. (Par. 16.)

A general discussion of the results is undertaken, in which the view is put forward that the absorption is determined by the formation on the walls of the vessel of electrically polar layers to which ions of the gas adhere in virtue of their charge. It is probable that it is the negative ions that adhere ; if this is so, an explanation can be offered of some apparently unconnected effects produced by the deposition of salts by the method of (6). In all that concerns the formation of the absorbing layer, phosphorus and the substitutes of (6) behave similarly. (Pars. 17–19.)

In other respects phosphorus (together with As, and probably S and I) has a specific action. The explanation of this action propounded in the previous papers is maintained. (Par. 20.)

The Quantity of Gas Absorbed.

1. The previous experiments had shown that if a given vessel is filled with gas mixed with phosphorus vapour and a discharge passed through it, the quantity of gas that can be absorbed depends on (1) the nature of the gas, (2) the quantity of phosphorus present, (3) the state of the walls of the vessel. It might also conceivably depend upon (4) the amount of gas originally present, (5) the nature of the discharge. If the form of the vessel is altered, it may also depend (6) on this form, even if its volume is constant. The possible effect (7) of the temperature has to be taken into consideration.

2. As to (1), the nature of the gas, the range open to investigation is very limited. Chemical compounds are excluded because they invariably undergo chemical change when the discharge passes, so that the great complications enter which have been fully discussed in the case of carbon monoxide. Of the elements, the inactive gases are known to be very little absorbed. Oxygen and the halogens attack metals, and especially the incandescent filament. The only remaining elements which have sufficiently high vapour-pressures at room temperatures are hydrogen and nitrogen. Hydrogen has been used throughout the greater part of these experiments, and "gas" will always mean hydrogen unless the contrary is stated. Observations on nitrogen have been made sufficient to show that in the absorption by means of phosphorus its behaviour is almost identical with that of hydrogen. In all cases a slightly greater volume of nitrogen than hydrogen can be absorbed; the difference amounts to about 10 per cent.; the variations in the amounts of the two gases absorbed as the conditions change are closely parallel, and no distinction between them need be made in respect of any of the conclusions which will be put forward.

3. In order to examine factor (2), the quantity of phosphorus present, it is practically necessary to use a new vessel for each experiment on absorption. In the first place,

it was found that the absorption of gas might change the state of the walls of a vessel in a manner not easily reversed, while no evidence could be found that all new vessels, suitably treated, were not in the same state ; the separation of factors (2) and (3) could be made with certainty only if no vessel was used for more than one absorption. In the second place, the easiest way to introduce into a vessel a known amount of phosphorus is to coat a wire with a known amount of red phosphorus, mixed with a trace of a " binder " to secure adhesion, and to heat the wire after it has been introduced into the vessel. (This process of coating wire with predetermined quantities of material is sometimes used in incandescent lamp manufacture and need not be described here.) Since ground joints are inadmissible in absorption experiments, on account of the inevitable presence of grease vapour, the wire had to be sealed in, and the renewal of the wire implies the renewal of the vessel.

Accordingly it was necessary to use vessels that could be readily obtained by the hundred. Ordinary incandescent vacuum lamps proved entirely suitable for the purpose. In such lamps the discharge which causes the absorption passes between the opposite ends of the filament, maintained at a difference of potential by the current which heats the filament; the negative end provides the requisite thermionic emission. In almost all the experiments 200–230 volt 40 watt lamps of the usual commercial type were used ; they had tungsten filaments about 1 metre long, about ·026 mm. in diameter in bulbs of about 210 c.c. volume.

It is difficult to coat filaments regularly with weights of phosphorus much less than 0·1 mgm. When smaller quantities of phosphorus were required, they were obtained by filling the lamp with gas, placing it in connexion with a vessel containing white phosphorus at a known temperature, and allowing time for the vapour of this phosphorus to establish its equilibrium pressure in the vessel. The estimation of the phosphorus introduced by this method requires a knowledge of the vapour-pressure of phosphorus at temperatures below that of the room ; the values assumed have been extrapolated (in a manner which will be described in another communication) from the data of MacRae and Van Voorhis *, which deal with temperatures above 44° C. It has been found subsequently in many of the experiments that this method is not wholly reliable, because if sufficient time is

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* D. MacRae and C. E. Van Voorhis, Am. Chem. Soc. J. xliii. p. 547 (1921).

allowed for true equilibrium to be obtained, there will be a large amount of phosphorus absorbed on the glass walls in addition to that present as free vapour. However, by choosing suitably the time of exposure, so that the equilibrium vapour-pressure is closely approached without considerable absorption on the walls, the amount of phosphorus introduced can be regulated with the accuracy required for these experiments. The greatest amount that could be introduced by this method, unless the whole system was artificially maintained at above the room temperature, which never exceeded 25° C., was 0·06 mgm.: by a combination of the two methods the whole range up to about 1 mgm. could be covered sufficiently.

4. Since the contamination of the gas with a continually renewed supply of mercury or grease vapour prevents all absorption, and since access of the gas to cooled traps would have removed all the phosphorus, it was necessary to conduct the absorption in a vessel completely sealed off. Two methods have been used for estimating the decrease of pressure, which alone can be used as a measure of the absorption that occurs. The first involved the use of the lamp filament as the hot wire of a Pirani gauge according to the method recently described by us *. The second depends upon a distinction between pressures which are above and those which are below the value at which the applied potential is equal to the glow potential. (I. 590; III. 228.)

The glow potential in a vessel, such as a lamp, having electrodes of which the area is very small compared with that of the walls, is the potential at which the current between those electrodes changes very suddenly from a small value, limited by the space charge and almost independent of the thermionic emission, to the value corresponding to the saturated thermionic emission, and therefore dependent on the temperature of the cathode. Suppose, then, that a lamp in which the pressure can be varied is connected in series with a similar but perfectly evacuated lamp in a Wheatstone bridge, the other arms being constant resistance coils. Whatever the pressure in the lamp, the bridge can be balanced for any constant applied voltage by adjusting the coils; but if the pressure in the first lamp is above that corresponding to the glow potential, the balance will change if the current through the bridge (and therefore the temperature of the filaments) is changed; for an increase of space

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* Research Staff of the G. E. C., London. Phys. Soc. Proc. xxxiii. p. 287 (1921).

current in the gas-filled lamp, due to increase in thermionic emission from the cathode, will not be accompanied by any increase in current in the vacuous lamp. On the other hand, if both lamps are vacuous, and their filaments approximately similar, the ratio of the filament resistance will hardly change with the current, and the very small space current will not change at all; the bridge will remain balanced while the current through it is varied over a considerable range. By means of this simple device of the two lamps connected in a bridge through which the current can be altered, it is a matter of a few seconds to determine whether the pressure in a lamp is above or below that at which the glow potential is equal to the applied potential. The glow potential varies so rapidly with the pressure in this region, and the pressure corresponding to the potentials used is so small (about ·0002 mm.), that for our purpose this pressure may be always taken as zero, independently of the applied potential. It may be remarked in passing that the disappearance of a visible glow is not always a safe test that the lamp is "cleaned-up," and that the pressure is below the critical value indicated by the bridge.

In order to measure by this method the quantity of gas that can be absorbed with a given amonnt of phosphorus, a series of lamps, each containing the same amount of phosphorus, is filled to a series of pressures. Each lamp is then "burnt" on the bridge in series with a perfectly evacuated lamp of the same type, and the division found between those which "clean-up" and those which do not. The pressure P at the point of division can be determined by some ten observations within 10 per cent. of its value; the mass of gas absorbed is then ρ V, where ρ is the density of the gas at pressure P and V the volume of the lamp.

5. It was established that P, corresponding to a given amount of phosphorus, was independent within wide limits of factor (5), the nature of the discharge producing the absorption. P did not depend on the voltage applied to the lamp, at any rate if this voltage was well above the limit at which appreciable thermionic emission from the filament begins. On the other hand, the time occupied by the absorption increased rapidly as the voltage, the temperature of the filament, and the space current were decreased. At voltages near the limit at which any discharge could be made to pass, it appeared that P decreased slightly, probably because, when the discharge lasts too long, the phosphorus accumulates in the parts of the vessel where no discharge

passes. Again, the substitution of a filament of half the length, designed for half the voltage, produced no change in P, nor did the use of a separate anode and cathode similar to the arrangement shown in fig. 1 of (I.). If electrodes of area comparable with that of the glass walls were used, such as those of a thermionic valve, changes in P undoubtedly occurred ; but they are to be attributed rather to changes in the form of the vessel than to changes in the nature of the discharge. In discussing the other factors, factor (5) may be left out of account.

It should be mentioned that experiments made on different batches of lamps, in all respects apparently the same, never agreed so perfectly in the determination of P as those made on a single batch. This variation is unexplained.

Factor (7), the temperature of the vessel, does not appear to be important, at any rate if the variation of the temperature is confined between 0° and 30° ; but no systematic observations on this matter have been undertaken. It is possible, but not probable, that some part of the unexplained variations are due to a secondary influence of temperature. Factor (6), the form of the vessel, undoubtedly has some effect ; it appears generally that the amount of gas that can be absorbed by a given amount of phosphorus increases somewhat with the area of the walls exposed to the action of the discharge. If the vessel in which the discharge takes place is merely connected by a narrow tube with another vessel, the weight of gas that can be absorbed with a given weight of phosphorus is unchanged ; but if the same electrode system (*e. g.* the lamp filament) is placed in a larger bulb of approximately the same shape, the weight absorbed with a given weight of phosphorus is increased. But again no systematic measurements have been undertaken.

6. There remains the important question whether P is really an adequate measure of the amount of gas that can be absorbed. It will be so only if the amount absorbed is independent of the starting pressures ; or, in other words, if, starting from a pressure $P+p$, the final pressure reached is always p, whether p is 0 (as in the method described) or is comparable with P. The experiments that have been made indicate that the amount absorbed is so independent of the starting pressure within wide limits. They were made by the use of the Pirani gauge. Table I. gives two typical series of results made in vessels of different volumes with different amounts of phosphorus. The first column gives the starting pressure $P+p$, the second the final pressure p, the

third the difference P. The variations between successive determinations are greater than can be attributed to experimental error in measuring the pressure, but there is no consistent variation of P with p.

TABLE I.

$P+p$. (Original pressure.)	p. (Final pressure.)	P. (Absorbed.)
0·491 mm.	0·457 mm.	0·034 mm.
·382	·330	·052
·293	·265	·028
·284	·250	·034
·233	·192	·041
·174	·139	·035
·119	·081	·038
·102	·053	·049
·093	·058	·038
·061	·032	·029
·035	·000	·035
0·150	·084	·066
·109	·040	·069
·094	·035	·059
·083	·032	·051
·068	·000	·068

It is apparently permissible to speak of a definite amount of gas absorbed with a given amount of phosphorus, independent both of the nature of the discharge and the pressure of the gas through which it passes.

7. If such independence is established, factor (2) can be isolated. Fig. 1 shows the relation, determined by observations on some 250 lamps by the method of Par. 4, between the amount of phosphorus introduced into the lamp and the amount of gas that can be absorbed, both amounts being expressed in milligrams. The points (×) joined by full lines were obtained when the experiments are conducted in the manner described. The features to which attention for subsequent discussion is drawn, and which are repeated in all other observations despite variations in detail, are:—(1) The general increase in the hydrogen absorbed with increase of phosphorus. (2) The maximum followed by a decrease. (3) The general slope of the line which, even if it were smoothed into a straight line, would not suggest any chemical combining proportions of the two elements, *e. g.* 10·3 to 1 (PH_3) or 31 to 1 (P_2H_2). (4) The marked "step" in the line from 0·09 to 0·27 mgm. of phosphorus; there are distinct indications of similar but less marked steps at the points for lower values, and even at the higher values considerable variations of the amount of phosphorus about

each point are not accompanied by proportional changes in the hydrogen absorbed; moreover there are some values of the amount of hydrogen absorbed which seemed never to occur however the amount of phosphorus was varied. (5) An amount of phosphorus below the step never gives a yellow coloration to the walls of the lamp after the gas has been absorbed, while an amount above the step always gives such a coloration.

The points marked ⊙ and joined by the dotted line were obtained by a slightly different procedure. Here, before the lamps were filled with gas, the filament was heated so as to deposit the phosphorus as a coloured film on the walls; the lamp was then filled with gas and the critical value of P determined in the usual manner. The observations were much less consistent than in the first series, the difference being probably due to the much longer time occupied in the absorption (see Par. 15), but the following features seem clear:—(1) The absorption is less than in the first series, especially at the higher values; (2) the maximum vanishes and is replaced by approximate "saturation"; (3) the marked step does not wholly disappear.

8. We now pass to factor (3), the state of the surface of the vessel.

In all experiments the walls of the vessel were freed from adhering gas (chiefly water and CO_2) by baking for five minutes to 400° C. during exhaustion. If this precaution is not taken, the absorption is less but results are irregular; doubtless the gas which is allowed to remain should be included in the amount absorbed. But if it is taken, the absorption is independent within very wide limits of the nature of the surface. Thus it is the same whether the vessel is made of soda, lead or borosilicate glass, or fused silica. It is unchanged by washing the surface with strong acids or alkalis; by etching it with hydrofluoric acid, liquid or gaseous; by sand-blasting it; or by depositing on it many salts by evaporation of solutions; it is little, if at all, changed by depositing silver chemically. In the examination of these modes of treatment some anomalies were found that have not been fully explained, but by none of them could the absorption be changed consistently[*].

On the other hand, there is a method by which the absorption can be greatly increased with perfect consistency. If

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[*] In II., p. 702, it was stated that P_2O_5 deposited on the walls of the vessel prevented absorption. This statement is not true if the material is thoroughly dried by baking and exhaustion.

the filament is coated with a suitable amount of certain salts, of which sodium fluoride is typical, in the same manner as it is coated with phosphorus for the experiments of Par. 7 ; and if, after the lamp has been baked and evacuated, the filament is heated for a moment to bright incandescence ; then it will be found that the amount of gas that can be absorbed with a given amount of phosphorus is very notably increased. Unless two filaments are sealed into the lamp, one coated with the salt and the other with phosphorus, it is necessary in making these experiments to introduce the phosphorus in the form of vapour. That method was adopted in all the measurements described below, and the amount of phosphorus which could be introduced was limited to about ·06 mgm. But it was found qualitatively that, if salt were mixed with phosphorus on a single filament, so that both were "evaporated" together, the amount of gas that could be absorbed was greater than if the same amount of phosphorus were present without the salt. But for reasons which will appear in the sequel, this method is not well adapted for quantitative investigation.

There is no doubt that the salt produces this increased absorption because it is deposited on the walls. It certainly is so deposited, because, if a large enough quantity is used, their lustre is changed. Moreover, if, after the filament has been heated, the lamp is opened, left exposed to the air for some hours, and then re-exhausted, the salt is still showing its presence by increased absorption. But if deposition of the salt on the walls by this method increases absorption, why does it not have the same effect when the deposition is effected by evaporating a solution? The answer is that the passage of the salt from the filament to the walls is not one of mere evaporation and condensation. Ionization is also involved ; for a visible glow is often seen to accompany the "evaporation," and electrical measurements show the passage of a current between cathode and anode, even when the greatest P.D. between them is less than 10 volts. There is also chemical resolution ; for the presence of free sodium, absorbing oxygen in the cold, can be detected after the heating of the salt ; but the presence of the sodium cannot be the determining factor, because the exposure to the air after "evaporation" does not affect the process.

9. Not all salts have been found to produce this increased absorption. Those that show it unmistakably are many

fluorides and chlorides, especially those containing sodium and lithium, silica, glass (the powdered material of the bulb), and sodium silicate. On the other hand, it has not been found with oxides, or with any of the halogen salts of potassium. Sulphates and some other salts cannot be tried because they destroy the filament. We have been unable to discover any relation between this property of salts and other properties, but we have some suspicion that the ionization potential of the ionized salt may be a determining factor, for slight traces of impurity, such as grease vapour or other hydrocarbons, may inhibit the effect even of those salts which normally display it. We are inclined to compare their effect with that of hydrocarbons or mercury vapour in inhibiting absorption of gas; the action ceases because the impurity of low ionization potential is ionized in preference to the salt vapour. However, this explanation is speculative.

In addition to salts, metallic tungsten from the filament itself may show the effect. If the lamp is burnt while it contains just enough gas to allow the glow discharge to pass, so that the walls become blackened with sputtered tungsten from the cathode end of the filament, the increased absorption in the presence of tungsten is obtained. In II., p. 689, we attributed the absorption of nitrogen in the absence of phosphorus to the sputtered tungsten; we believe that the presence of this material is the reason why the absorptive power of the walls of the vessel is changed apparently by the process of absorption (*cf.* II., p. 703) so that it is necessary to use a new vessel for every experiment.

It should be mentioned that the enhanced absorptive power due to the salt is exhausted by absorption. If a vessel in which salt has been "evaporated" and gas subsequently absorbed is re-filled with gas, after the usual baking and evacuation, the absorption on the second occasion will be much less than on the first, and on the third will not be different from that of a normal glass vessel. This fact is not inconsistent with the view suggested in the last paragraph of the action of sputtered tungsten; for in that case fresh sputtered tungsten is being deposited while the previous layers are being used up.

10. Measurements have been made of the amount of salt necessary to produce the increased absorption. The following figures give the results of a series of trials with

sodium fluoride, the amount of phosphorus introduced being always ·05 mgm. :—

NaF coated on wire (mgm.).	Hydrogen absorbed (mgm.).
0	·0007
0·09	·0007
0·2	·0007
0·28	·0019
0·36	·0023
2·0	·0023

Almost all the effect is obtained by an increase from 0·2 to 0·28 mgm. Similarly with silica and sodium silicate, it occurred between 0·3 and 0·35, but with lithium fluoride below 0·17 mgm. It is natural to inquire whether the critical amount is that required to form a monomolecular layer on the surface of the glass. The area of this surface was about 200 cm.^{2}; the area of a molecule of NaF is about 4×10^{-16} cm.^{2}; consequently to form a monomolecular layer about 0·035 mgm. would be required. This is only about one-eighth of the experimental value; but it is clearly possible that all the salt introduced is not deposited uniformly on the walls in the active condition.

11. Inquiry was also made how the presence of the active film affected the relation between gas absorbed and phosphorus present, examination being confined to quantities of phosphorus below the step in fig. 1. The significant result was obtained that, in the presence of salt, any of the points below the step (except possibly those corresponding to less than 0·02 mgm. of phosphorus) might be raised to the step at ·0023 mgm. of hydrogen. The maximum effect was not always obtained, but the maximum obtained with any given salt and any given amount of phosphorus appeared quite independent of the nature of the salt (so long as it would produce the effect at all) and almost independent of the quantity of phosphorus; moreovor, this maximum was the same within the limit of error as the step of the phosphorus line.

Some less systematic observations will now be described which provide additional evidence on which to base a general discussion.

Absorption without Phosphorus.

12. Even when no phosphorus is present, the burning of the lamp and the accompanying discharge produce some absorption of gas. But unless the original pressure is very

low (say less than ·005 mm.), the pressure never falls below that corresponding to the glow potential, and a complete clean-up is never indicated by the bridge method of Par. 4, even though the amount of gas that can be absorbed, starting from a higher pressure, is much greater than that corresponding to a pressure of ·005 mm. During the first minute of the burning, the pressure falls by an amount which depends somewhat upon the original pressure, but is about ·02 mm.; subsequent changes are much slower. In some cases the pressure begins to increase again very slowly, and will continue to increase until the filament finally fails; in other cases it will continue to fall very slowly, the fall always being accompanied by a marked blackening of the bulb and being due presumably to sputtered tungsten (*cf.* Par. 9). The cause of the difference has not been fully ascertained, but it is suspected that the rise occurs when the gas is more highly contaminated with grease vapour, some of which may be admitted during filling. But in both cases there is evidence that gas is being evolved as well as absorbed, for even if no water vapour is initially present, a trace of it can often be found in the later stages, in spite of the presence of the incandescent tungsten.

If the wire is originally coated with one of the active substances mentioned in Par. 9, an appreciable absorption of gas occurs during the first instant of burning and while the glow lasts, which is the sign of the "evaporation" of the salt. This absorption may amount to ·03 mm., and is as much as ·015 mm. in argon—a gas which shows no absorption comparable with this in the other circumstances of these experiments. After this initial stage, or if the salt is evaporated from the wire before the lamp is filled with gas, the absorption during the burning of the lamp is definitely greater than it is when no salt is used. Moreover, the absorption is never reversed. It is still true that a perfect clean-up, indicated by the bridge, is never attained, but otherwise the salt acts in much the same way as it does in the presence of phosphorus. In fact, after salt has been deposited, the amount of gas that can be absorbed is approximately independent of the original pressure (as it is when phosphorus is present); and the amount of gas that can be absorbed is not very different from that corresponding to the step of fig. 1 which, when salt is present on the walls, gives the absorption for almost all quantities of phosphorus below a certain limit; it appears, however, that the presence of a little phosphorus is necessary to give the full value of ·0023 mgm. in fig. 1.

The Rate of Absorption with Phosphorus.

13. Just as there is a very rapid absorption of gas at the moment when salt is evaporated from the filament in the absence of phosphorus, so there is a very rapid absorption when phosphorus is evaporated from the filament in the absence of salt, or at the moment when phosphorus, present originally as vapour, is deposited on the walls as red phosphorus by the starting of the discharge. Accordingly, even when phosphorus is used without salt, the absorption takes place in two stages, unless the phosphorus is first deposited on the walls as described in Par. 7 ; the first stage is practically instantaneous and is impossible to control ; the second is very much slower. The ratio between the amounts absorbed in the two stages differs, as might be expected, with the initial pressure ; as this pressure is increased, the amount absorbed in the first rapid stage is increased relatively to that absorbed in the second slow stage. But, as noted previously, the sum of the two amounts is approximately independent of that pressure.

Attempts have been made to relate the rate of absorption to the ionization in a manner similar to that adopted in (III.), but they have met with no success. Indeed, the experiments of (III.) indicate that, even if the experimental difficulties could be overcome, the interpretation of the measurements would be very complex. For it was shown there that, in order to obtain any simple relation between ionization and absorption, it was necessary to suppress, as far as possible, recombination and the arrival of positive ions at the cathode. During the very intense ionization that accompanies the first stage of the absorption, recombination is unavoidable ; in the second, either the ionization is very much greater than that found permissible in (III.), or the absorption is so slow that the disturbing factor mentioned in Par. 5 enters. Moreover, the theory of the action that has been proposed, and is confirmed by the experiments of this paper, indicates that the action which produces absorption takes place, not in the gas as in (III.), nor even at the metallic electrodes, but at the glass walls which are acting as electrodes of both signs. In such conditions the difficulties of interpretation would be enormously increased.

All that has been achieved is a demonstration that, in any particular conditions of pressure and state of walls, the rate of absorption is approximately proportional to the ionization. But the only conclusion which it seems permissible to draw from that fact is that absorption is not an action requiring the meeting of two or more charged particles.

Absorption without the Glow.

14. In (I.) and (III.) it was stated that (in the absence of phosphorus) no absorption took place unless the potential driving the discharge was greater than the glow potential. Of course this statement, interpreted literally, is not true; for it is well known that absorption occurs in X-ray tubes and other high-vacuum apparatus at pressures far below that at which the applied potential will maintain a visible glow. But it is true that, at the pressures of a few hundredths of a millimetre with which we were there concerned, the absorption without the glow is so slow that it cannot be detected by the method employed, and that, when the glow appears, the rate of absorption increases enormously. The explanation of the glow potential given in (III.), p. 33, shows that the attainment of the glow potential and the appearance of the glow are accompanied by an enormous increase in ionization, and that the doubt on this point expressed in (I.) was unjustified. Accordingly if, as all our experiments indicate, absorption and ionization are intimately connected, it is to be expected that the absorption which accompanies the glow will also occur, though at a much less rate, with potentials less than the glow potential, so long as they are above the ionization potential.

The ratio of absorption to ionization is very much greater in the presence than in the absence of phosphorus vapour *; and it seemed possible that perceptible absorption might occur in its presence, even with potentials too small to cause the glow. The expectation has been fulfilled. The experiments were conducted partly with a vessel like that of fig. 1 in (I.), partly with lamps designed for very low voltages (less than 30). It was found, as was to be anticipated, that the first stage of the absorption discussed in Par. 13 was little affected by the potential between the electrodes, and that a notable absorption always occurred at the moment of lighting the filament, if it had been coated with phosphorus or the gas mixed with phosphorus vapour. But the second stage occurred also, and a perceptible absorption would continue after the first stage was ended, although no glow was visible and electrical measurements showed that the current was limited by the space charge

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* This statement is not certainly established. It is certain that the absorption corresponding to a given electron current from the cathode is much greater if phosphorus is present; but the phosphorus appears to produce some increase of ionization as well as of absorption.

rather than by the temperature of the cathode; the process differed from that associated with the glow only in being much slower.

The question was therefore raised at what pressure the absorption ceases. If absorption is due to ionization, it should continue indefinitely, even at the very lowest pressures, so long as the applied potential is greater than that required for ionization. Experiments, which need not be described in detail, confirmed this view. The absorption of gas in the high-voltage lamps which were used in the main experiments does not cease when the glow disappears and when the bridge of Par. 4 shows a complete "clean-up." If an ionization gauge, adapted for very low pressure, is used, the pressure will be found to decrease continually, but with continually decreasing speed, until the limit of the gauge is reached. If the usual precautions against the evolution of gas from the metal parts are adopted, a vessel can be evacuated until it shows the characteristics of Langmuir's "high vacuum" by simply connecting it to an ordinary incandescent lamp burnt at its normal voltage; but the exhaustion, even if the volume of the vessel is small compared with that of the lamp, may take several days.

On the other hand, no indication has ever been found of absorption at potentials too small to cause ionization. Experiments on this matter must be made on nitrogen, on account of the peculiar property of hydrogen in disappearing without ionization (*cf.* II., p. 686). It appears that ionization of the gas, and possibly of the phosphorus, is the one condition necessary for the absorption to occur. Some abortive attempts have been made to establish this proposition more certainly by ionizing a gas at atmospheric pressure by ionizing rays; but the proportion of the molecules that can be ionized in any finite time by such a process is so small that success was hardly to be expected.

Destination of the Gas.

15. Though all the evidence goes to prove that chemical action in the ordinary sense plays at most a secondary part in the absorption, it was thought desirable to trace as far as possible any chemical changes that take place. The gases in the lamps used in the absorption experiments were analysed by the method recently described by us *. The only gases which have ever been identified in the lamps, besides

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* Research Staff of G. E. C., London. Phys. Soc. Proc. xxxiii. p. 287 (1921).

those with which they were filled, are H_2O, CO_2, PH_3, and (when nitrogen was used) NH_3. Since the "condensation point" of all these gases is above liquid-air temperature, they can be detected certainly if their partial pressure is above ·0005 mm. in the presence of 0·1 mm. of non-condensible gas. No other gases with condensation points above that temperature were present. This conclusion is important, for it seems to dispose of the hypothetical compounds of extraordinary constitution that have sometimes been imagined to account for the absorption.

If the process of absorption was interrupted after the first stage of Par. 13 (which cannot be subdivided), no gas was ever found except hydrogen or nitrogen. The phosphorus vapour disappears during the first stage, and no compounds are present in the gas in appreciable amount. This observation does not prove that compounds are not formed, but only that, if they are formed, they are absorbed as fast as they are formed.

The restoration of the absorbed gas on heating the vessel was partially described in (II.). Much more complete observations have now been taken, the results of which will be summarized. The great difficulties in drawing certain conclusions from these experiments are (1) that at the temperatures necessary for the permanent restoration of the gas, there is an almost inexhaustible evolution of water and CO_2 from the vessel, even if it has been thoroughly baked and exhausted beforehand and no discharge has passed through it*; (2) that the temperature necessary for restoration may change the nature of the gas restored. (1) can be avoided to a great extent by always comparing the gas obtained from the vessel in which gas has been absorbed with that from a precisely similar vessel treated similarly in which no gas has been absorbed.

At room temperatures the absorption is quite permanent; vessels have been kept for a year (without the passage of a discharge which might absorb again the gas restored), and at the end of that period have shown no signs of the restoration of gas to the most sensitive tests. Heating the vessel to 100–120° C. causes some restoration of gas, which disappears again when the vessel cools. The first permanent evolution of gas occurs at about 180° C., but the evolution is not rapid until 300° is attained; at 350° the restoration is effected in a few seconds. Permanent restoration is always accompanied by the appearance of phosphorus

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* R. G. Sherwood, Phys. Rev. xii. p. 448 (1918).

vapour; it seems, therefore, as stated before (II., p. 699), that the evaporation of the deposited phosphorus is necessary for that restoration. In addition to phosphorus, hydrogen, water, and CO_2 always appear, even if the vessel was originally filled with nitrogen; if it was so filled, nitrogen appears *. The presence of CO_2 is an almost certain proof that these gases are derived from the glass. Since they are produced in greater quantity than if the discharge has not passed, it may be concluded that they are produced by the discharge, the hydrogen being reduced from water by the filament. The liberation of gas from the glass, even while absorption is going on, seems inevitable; it doubtless accounts in part for the fact that, if the absorption is very slow, the amount of gas that can be absorbed is less (*cf.* Par. 7). PH_3 appears fitfully in small amounts, never exceeding 15 per cent. by volume of the "restored" gas. It is known that PH_3 dissociates at the temperatures used in restoration, and it was thought at first that its small and variable amount might be due to varying extents of dissociation; but when it appears, its quantity is not greatly changed by a further maintenance at the highest temperature reached during restoration; it appears to be in equilibrium with the P and H also present. NH_3 has sometimes been detected when nitrogen has been absorbed; but its amount is again small and variable.

When hydrogen has been absorbed, it is difficult to tell under what conditions it is all restored, owing to the admixture of hydrogen compounds from the glass. But when nitrogen has been absorbed, this complication does not enter, and it can be established within an error of some 10 per cent. that the gas restored by heating for a few minutes to 300° is equal to that absorbed, so long as the absorption has been effected by phosphorus. If, however, the nitrogen has been absorbed by evaporating salt from the wire, as described in Par. 12, little, if any, of the gas can be restored,

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* In II., p. 700, it was stated that nitrogen absorbed in the presence of phosphorus could not be restored by baking. But in those experiments the vessel was always filled with more nitrogen than the phosphorus would absorb, and a glow discharge continued through the remaining gas for some time after the absorption was really complete. In these circumstances there is much sputtering of the cathode, and, as suspected before, the layer of phosphorus and absorbed gas becomes coated with involatile tungsten. In these experiments, on the other hand, the nitrogen originally present was completely absorbed in a few seconds and there was no appreciable blackening of the bulb; accordingly the gas could be restored by baking.

even by heating the glass to near its softening temperature. The same appears to be true when hydrogen is absorbed; but, for the reasons explained, the conclusion is less reliable. These observations indicate again that the removal of the solid layer in which the gas is absorbed is necessary to the restoration of the gas. There is similar evidence that, if salt and phosphorus are evaporated together from the wire, some of the phosphorus is so entangled in the salt that it is permanently removed from the action. This is the reason why quantitative experiments in which salt and phosphorus are evaporated together are unreliable (*cf.* Par. 8).

One further fact may be noted. The gas restored by heating does not depend on the pressure of the gas in the lamp during absorption. Even when this pressure is as great as 0·5 mm., if the unabsorbed gas is pumped out completely and the lamp then sealed off and heated, the gas restored is indistinguishable from that which would have been obtained if the absorption had taken place from a pressure so low that all the gas originally present could be absorbed. Even at a pressure so high that the free path of ions is very small compared with the dimensions of the lamp, the absorbed gas is to be found on the walls of the vessel.

16. Whitney has shown [*] that other substances than phosphorus possess much the same specific action in promoting absorption, namely sulphur, iodine, and arsenic. The first two we have not investigated, but we can confirm his conclusions that the behaviour of arsenic is indistinguishable from that of phosphorus in most of the matters discussed here. All these substances resemble each other in being elements and so not decomposed by the discharge, and in having more than one allotropic modification. The bearing of the last property will be evident from our suggestions in Par. 20.

General Conclusions.

17. We do not profess to offer a complete theory of all the observations that have been described. But it seems to us clear that the suggestions as to the action of phosphorus in promoting absorption, which were offered in III. p. 704, are generally confirmed. The action of this substance is due to

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[*] *Cf.* S. Dushman, General Electric Review, xxiv. p. 680 (1921).

the formation of a layer of red phosphorus * on the walls of the vessel under the action of the discharge, and the gas absorbed is held by this layer. On the other hand, the view that the layer merely acts by protecting the absorbed gas from further bombardment is probably too crude. For the experiments with salts or tungsten evaporated from the filament show that layers of these substances on the walls promote absorption in a manner very closely similar to that characteristic of phosphorus. Since there is no reason to believe that these substances, once deposited, can be removed and deposited again (as suggested in II., p. 698), the gas that is held by these layers must lie above rather than below the layer. The view to which we incline now is that solid films deposited on the walls from ionized molecules under the action of the discharge are in an electrically polar condition ; they may perhaps be regarded as bearing a free charge on their surface. When gaseous ions suitably charged approach this polar surface, in virtue of their charges they enter into a combination with it and cannot be liberated again except by a considerable rise of temperature. The action is similar to that which Langmuir has imagined for the explanation of so many surface actions. This supposition will form the basis of our discussion.

18. First it should be noted how completely similar, up to a certain point, is the action of phosphorus and of the salts (a term which, for brevity, will be used to include tungsten). The "first stage" of Par. 13 in absorption by phosphorus (which alone will be discussed for the moment) corresponds exactly to the absorption of gases in the absence of phosphorus by evaporating the salts in their presence (Par. 12). The quantities absorbed in this stage depend so greatly on the pressure of the gas and other factors that quantitative comparison is difficult ; but the amounts absorbed in the two cases under comparable conditions are not very different.

Again, the amounts of gas that can be absorbed by a layer of phosphorus and by a layer of salt are very similar. It is natural to identify the step of fig. 1 with the amount that can be held by a single complete layer of phosphorus, and this step is very nearly, at least, the amount that can be held

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* In speaking of "red" phosphorus, we do not mean to commit ourselves to the view that the element is present in the molecular condition characteristic of red phosphorus in bulk. We only mean that it is present in some condition differing, like that of red phosphorus, from the white variety in the fact that the vapour-pressure is inappreciable at room temperature.

by a layer of salt, whatever its chemical nature. Further, the phosphorus curve rises to the step with increase in amount of phosphorus nearly as steeply as the amount absorbed by salt ; in fact, we have never been able to satisfy ourselves that there can be absorbed by phosphorus an amount of gas intermediate between that which can be absorbed by plain glass and that corresponding to the step. (The difficulty of deciding the matter is that, if neither salt nor phosphorus is present, the absorption is not determinate, but represents an equilibrium between absorption and liberation by decomposition of the glass under bombardment.) It is not at all clear why the increase in absorption up to the step caused by salt or phosphorus is discontinuous; for, according to the theory proposed, it might be expected that quantities of material insufficient to cover the walls completely would cover them partially and so give an intermediate absorption. It is possible that, if the walls are not completely covered, absorption is again masked by liberation of the gas from the glass; but the difficulty, whatever its explanation, is the same for phosphorus as for salt. The increase of absorption with quantities of phosphorus greater than that required for the step, which is not shown by salt, will concern us presently.

The quantity of gas absorbed at the step is not very different from that corresponding to a monomolecular layer. The calculated amount is ·0016 mgm. (or ·0008 if the layer is monatomic), the observed ·0023. The discrepancy is explicable if the molecules present to the surface a diameter less than that estimated by the usual methods, or, in other words, if the molecules are attached "end-on." The view that molecular layers are concerned would explain the close similarity between the *volumes* of nitrogen and hydrogen absorbed in similar circumstances.

19. If this general view is correct, it is natural to inquire in which direction the polar layer is directed and ions of which sign enter into combination with it. The very small absorption of the inactive gases, which do not form negative ions, suggests that it is negative ions which are absorbed by the layer. We have not been able to devise an experiment to test this point, but there is some indication from another source that layers of salt, deposited as we have described, are able to bind negative charges. For Hamburger and his associates have shown * that layers of salt so deposited have

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* L. Hamburger, G. Holst, D. Lely, E. Oosterhuis, *K. Akad. Amsterdam Proc.*, Sept. 21, p. 1078 (1919).

the power of decolorizing tungsten subsequently deposited on them. They attribute the action to the formation of large molecular aggregations of the metal which cover but a small part of the surface, but they produce little evidence for their view except a proof that the action cannot be due to the formations of chemical compounds, as had been imagined previously. Now, the decolorizing of tungsten might be effected merely by the binding of the free electron and the transference of absorption to a definite region in the ultra-violet, similar to that of most chemical compounds in which the electrons are "bound"; and it is known that films of tungsten too thin to show appreciable absorption in visible light show strong absorption of ultra-violet light. We suggest tentatively that this decolorization of tungsten is physically the same process as the absorption of gas; both represent the binding of a negative charge on an electrically polar layer. Whether such binding is to be called "chemical combination" is a question of words; we prefer (*cf.* I., p. 586) to confine the term "chemical" to cases where separable compounds of fixed constitution are found, obeying the law of constant proportions. But the action would, in our view, be "chemical" in the sense employed by Langmuir in his theory of surface actions associated with monomolecular films.

Perhaps we may proceed further. In II., p. 703, we suggested that there is only one reason for believing that the action of phosphorus in promoting absorption is "chemical," namely that the absorption of gas decolorized the yellow film of phosphorus on the walls. If the colour is associated with the positively charged portion of the phosphorus molecule, the binding of negative charges on the layer might well decolorize it. Once more, if this explanation of the matter is correct, absorption by phosphorus is closely related to chemical action; but it is not chemical in the sense that any compound of phosphorus and the gas in definite proportions is ever free from atoms of those elements in the "uncombined" state.

20. We have so far discussed actions in which salt and phosphorus can be mutual substitutes. But the salts do not possess all the properties of phosphorus in the promotion of absorption. With phosphorus, but not without it, pressures well below the glow potential can be reached starting from pressures well above it. On this matter we have nothing to add to the explanation offered in II., p. 697, based on the

wide difference between the rising and falling glow potentials of phosphorus vapour. The other differences are probably due to the fact (II., p. 698) that phosphorus once deposited on the walls can be liberated and re-deposited under the action of the discharge, while salt cannot. This re-deposition doubtless accounts for the increase in absorption beyond that corresponding to a single layer obtained when the amount of phosphorus is increased beyond that required for a single layer, even if the phosphorus is deposited on the walls before the absorption begins (see the dotted line of fig. 1). The form of the full-line for the larger quantities of phosphorus is more difficult to explain in detail, for here the first stage of Par. 13 as well as the second is concerned; it is not unreasonable on any theory to imagine that the absorption will be greater when the gas is actually mixed with a large proportion of the vapour being deposited. The decreased absorption with the largest quantities of phosphorus, of which we are sure experimentally, we attribute to the fact that, when such large quantities are used, the number of phosphorus molecules present in the lamp just after evaporation is much greater than the number of gas molecules. In these circumstances the phosphorus molecules rather than those of the gas are ionized, and it is the former rather than the latter which are deposited on the walls.

21. Finally, there remains the question of absorption without either phosphorus or salt. Is this also to be attributed to an electrically polar layer on the glass surface? We imagine that it is; for all surface layers are bound to be electrically polar to some extent, since the elementary charges are not coincident. There is also the possibility that the surface layer is rendered polar by the action of the discharge, which also ionizes the molecules and makes them able to adhere to it. Against this latter suggestion is the fact, apparently ascertained, that the absorption takes place on portions of the walls which have not been exposed to the discharge, at least as readily as on those so exposed. But all these matters require further investigation.

XCIX. *An Attempt to detect Induced Radioactivity resulting from α-Ray Bombardment.* *By* A. G. Shenstone, *B.A.* *

IN recent experiments † Sir Ernest Rutherford and Dr. Chadwick have shown that a certain proportion of collisions of α-particles with atoms of some of the lighter elements causes the ejection by the nucleus of charged particles which can be identified as hydrogen nuclei. From the consideration of their energy of emission, it is shown that these particles must have derived a portion of their energy from the internal energy of the original nucleus. Moreover, the work of Dr. Shimizu ‡ in the Cavendish Laboratory on the photography of the tracks of α-particles in saturated air suggest that a much larger proportion of α-particles, of the order of 1 in 300, produces some other form of separation of the constituents of the nucleus. In some cases this action is apparently the ejection of a helium nucleus.

Such facts have very materially increased our knowledge of the structure of the atomic nucleus. But, because of our almost complete ignorance of the forces existing in and immediately around the nucleus, no definite deductions can be drawn as to the subsequent history of the nucleus from which a portion has been ejected.

It would seem, however, that such a violent partial dismemberment of a composite system could not fail to have still more far-reaching results. The stability of the nucleus cannot fail to be upset to some extent; and lack of stability in the nucleus is, we believe, essentially the cause of radioactivity. The critical point is the degree of that instability. It may be so great that the nucleus is completely and instantaneously dismembered; or it may be so small that the atom almost immediately regains equilibrium in a new form. The existence of isotopes of many elements is strong evidence that the latter condition is quite probable. Between these two extremes, however, is the whole range of degrees of instability exemplified in the radioactive substances.

If the effect of the condition of the deranged nucleus is the further emission of high-speed particles after a time of the order of hours or minutes, it would almost certainly have

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* Communicated by Prof. Sir E. Rutherford, F.R.S.

† Roy. Soc. Proc. A. xcvii. p. 374 (1920); Phil. Mag. Nov. 1921.

‡ Roy. Soc. Proc. A. xcix. p. 432 (1921).

been detected before now; but if the time is of the order of a small fraction of a second, it would not have been differentiated from the direct effect by any experiments so far performed. The present experiment was therefore carried out to extend observations down to a time-interval that would correspond to very rapid changes.

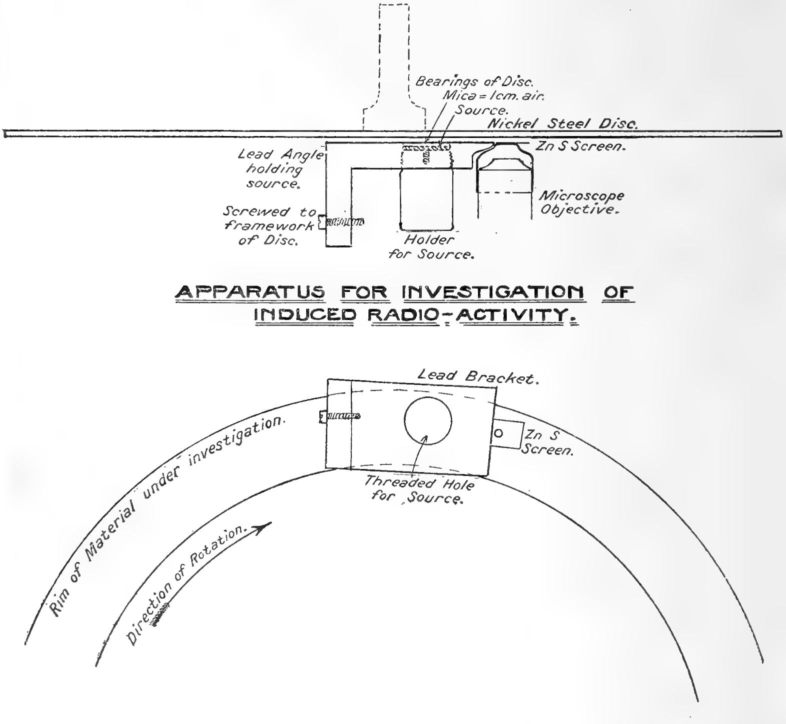
There were two essentials governing the experimental arrangement used to attack this problem. The first was a very short time interval between the α-ray bombardment and the observation. The second was the smallest possible space-interval between the bombarded atoms and the observing device in order to detect particles of short range. The scintillation method was used, and the problem therefore narrowed to the detection of particles of mass and velocity capable of producing a scintillation comparable with the H-scintillation.

The small time-interval was obtained by the use of a nickel steel disk of 8 inch diameter which could be rotated at a very high speed. The time-interval between the bombardment of a point on the wheel and the observation on that point can then be made extremely small by making the distance between bombarding source and observing-screen very small and the speed of the wheel very large.

After a few minor difficulties, the final arrangement of the source of α-rays and of the observing-screen was essentially as shown in the attached diagram. A lead bracket having a half-inch hole was screwed firmly to the framework holding the wheel so that its surface was about 1 to $1\frac{1}{2}$ mm. from the face of the steel disk. The metal source was of 1·2 cm. diameter, and was arranged to be held in the hole of the lead bracket with its active face about 2 mm. from the surface of the steel disk. It was found necessary to protect the active material from the draught caused by the disk when at high speed in order to prevent contamination of the disk itself. A thin sheet of mica of stopping power equal to ·9 cm. of air was accordingly waxed over the opening in the lead bracket. It was unfortunate that this was necessary, since it cut down the range of the α-particles to 6·06 cm. and consequently reduced their effective energy.

The distance between the source and screen was limited by two factors; a certain minimum thickness of lead was required to cut down γ-radiation and so fluorescence of the screen; and it was necessary to separate source and screen sufficiently to prevent the possibility of too many hydrogen particles directly ejected by oblique α-particles from reaching the screen. This distance in practice was 1·2 cm. Actually with the arrangement of distances such as is shown in the diagram a few hydrogens could reach the screen. With aluminium they were observed about 1 in 6 or 7 minutes whether the disk was running or stationary. To avoid vibration the ZnS screen was mounted on a very stiff attachment on the microscope objective, and remained in perfect focus even when the vibration was at its worst.

Fig. 1.



Difficulty was had at first from the wind from the disk blowing the crystals off the screen, but this was satisfactorily overcome by covering the screen with aluminium foil except for a hole over the portion included in the field of the microscope. The microscope used was fitted with Watson's "Holos" × 5 eyepiece and Holos objective of ·45 n.a. and 16 mm. focal length. A rim of the substance under examination was stuck on to the face of the wheel with shellac, which successfully withstood the huge centrifugal force except in the case of lead foil. After one accident it was not thought advisable to run more than $\frac{2}{3}$ max. speed with lead.

With the available driving apparatus it was possible to drive the steel disk at a speed of 250 revolutions per second. Taking the circumference for the bombarded portion of the wheel as 60 cm., this gives a velocity of 15,000 cm. per sec. Since the distance between the edge of the active source and the screen was 1·2 cm., the time for the wheel to move between these points is $\frac{1}{12,500}$ sec. But from the diagram it is evident that the heavily though obliquely bombarded portion of the wheel has to move through only about ·5 cm. in order to reach a position where it can in turn bombard the screen. This gives a time-interval of $\frac{1}{30,000}$ sec.

The observations were first made with the wheel stationary or running very slowly, and the numbers of natural scintillations counted. Except in the case of lead, these never amounted to more than 1 in 2 minutes. The wheel was then gradually speeded up and the screen observed as far as possible continuously. The roar of the wheel when running at high speed was not, at first, conducive to perfect concentration on the observer's part ; but, after one experiment had been carried out in safety, no further difficulty was experienced.

The materials tried included a wide range of atomic weights. The first tried was carbon in the form of paper. No effect at all was found. Aluminium, because of its proven emission of H particles, was considered a very likely material, but from it also no effect was observed. The wheel itself, of nickel steel, was next tried ; but, like the others, it gave no observable emission. The lower limit of observation in these experiments was probably one scintillation a minute. Two would most certainly have been detected. In the case of lead, however, the number of natural scintillations observed was as high as three a minute, so that the limit of detection of additional scintillations was probably not better than three a minute. With lead no effect at all was observed with the disk running about 160 revolutions a second.

A rough calculation shows that the period of decay of the induced radioactivity, if it exists at all, must be extremely short to have remained undetected. Sources of about 25 to 30 mgs. activity were used. Assuming that $\frac{1}{10}$ of the α-particles could reach the disk and that 1 in 10^6 ejects a portion of the nucleus, the number of abnormal atomic nuclei produced per minute is

$$\frac{25\times 3{\cdot}7\times 10^7\times 60}{10^6\times 10}=5500.$$

Roughly 1 in 250 of the particles which might be emitted by the abnormal atoms would strike the ZnS screen if the screen were directly over the bombarded portion. Assuming that the number of particles emitted decreases exponentially with the time and that one α minute could be detected, the time between bombardment and observation must have been at least four times the half-period of decay of the substance. This gives a maximum half-life of $\frac{1}{12,500}\times\frac{1}{4}=2\times 10^{-5}$ sec.

The above calculation makes use only of those atoms changed by the ejection of an H-particle. If the variety of disruption observed by Mr. Shimizu is included, the minimum observable half-life is considerably decreased since the number of abnormal nuclei is now

$$\frac{25\times 3{\cdot}7\times 10^7\times 60}{10^2\times 10}=55\times 10^6 \text{ per min.}$$

But $$\frac{55\times 10^6}{250}\times\frac{1}{2^{17}}=1{\cdot}7.$$

Therefore the maximum half-life becomes

$$\frac{1}{12,500}\times\frac{1}{17}=4{\cdot}7\times 10^{-6}\text{ sec.}$$

In order to examine the possibility of a cumulative effect from a long, heavy bombardment by the α-particles, an arrangement was made by means of which a metal strip, after several minutes' bombardment, could be brought beneath the ZnS screen after an interval of about $\frac{1}{100}$ sec. This likewise gave no observable result.

The negative results obtained in these experiments do not, of course, preclude the possibility of radioactive disintegrations taking place which involve the emission of β-particles, γ-radiation, or of mass particles of range less than 2·0 mm. But the evidence is very strong, in the case of aluminium, carbon, and iron, that no mass particles of range greater than 2·0 mm. are produced after an interval of 8×10^{-5} sec., and that none of range greater than 6 mm. are produced after an interval of $3{\cdot}3\times 10^{-5}$ sec. The corresponding intervals for lead are $1{\cdot}2\times 10^{-4}$ and $5{\cdot}0\times 10^{-5}$.

It is very unfortunate that time did not permit of further experiments with a wider variety of elements and with devices for the detection of radiation of other kinds. The importance of a complete investigation arises from the fact that the tracing of the subsequent history of the atomic nucleus which has been disrupted by the collision of an α-particle is, at present, one of our few paths to a knowledge of the forces within the nucleus.

In conclusion, I wish to thank Sir Ernest Rutherford for giving me this very interesting problem ; and Mr. Bieler for his assistance during observations.

Cavendish Laboratory,
Cambridge, 1921.

C. *On the Appearance of Unsymmetrical Components in the Stark Effect.* *By* A. M. Mosharrafa, *B.Sc.*[*]

§ 1. *Preliminary.*

THE theory of spectral lines which has hitherto proved most successful in interpreting the results of experiment is based upon certain assumptions of a quantum type introduced by Bohr [†], Sommerfeld [‡], and others. Such assumptions are only justifiable in so far as they give satisfactory interpretations of correlated phenomena. The effect of an electric field upon spectral lines emitted by substances subjected to the field was first investigated by J. Stark [§] in 1913 ; and an approximate theory was furnished by K. Schwarzschild [||] and by P. Epstein [¶] independently in 1916 : the two theories are similar and give satisfactory explanations of the phenomenon as investigated by Stark. *Now, according to their theory, the components into which any given spectral line is split up are symmetrically distributed about the original position of the line.* In the

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[*] Communicated by Dr. J. W. Nicholson, F.R.S.

[†] See *e.g.* N. Bohr, "Constitution of Atoms and Molecules," Phil. Mag. July 1913.

[‡] See Arnold Sommerfeld, 'Atombau und Spektrallinien,' II. Auf. (1921).

[§] *Berliner Sitzungsber.*, November 1913 ; *Ann. d. Phys.* xliii. p. 983 (1914).

[||] K. Schwarzschild, "Zur Quantentheorie," *Berliner Sitzungsber.*, April 1916.

[¶] P. S. Epstein, "Zur Theorie des Starkeffektes," *Ann. d. Phys.* l. p. 489 (1916).

present paper a closer approximation is worked out, and it is found [see § 4] that for stronger fields than those used by Stark this symmetry no longer follows from the theory: on the other hand, a pair of components which, for fields comparable with those that Stark used *, appear symmetrically situated, would for stronger fields be displaced *in the same direction*, so that the symmetry is destroyed. We, naturally, also find that the relation between the strength of the field and the displacements of the lines is no longer represented graphically by straight lines, but by parabolic curves whose curvatures change sign with the displacements (*i. e.* displacements of opposite signs correspond to parabolas of opposite curvatures).

It appears to the present writer that an experimental investigation of the Stark effect for fields stronger than those that have already been employed by Stark is highly desirable as a further test of the fundamental hypotheses of the quantum theory of spectra: if such an investigation result in the verification of the predictions already referred to, then this will add to our faith in the foundations of the quantum theory of spectral lines: whereas a negative experimental result would, unless the analysis here presented be at fault, lead us to a reconsideration of our assumptions, and perhaps to certain modifications thereof.

§ 2. *Previous Work.*

The equations restricting the motion of an electron moving under the influence of an attraction towards a nucleus as well as a fixed force F can be written in the form

$$\left.\begin{aligned} J_\xi = \int_0 \sqrt{f_1(\xi)}\, d\xi = n_1 h, \qquad J_\eta = \int_0 \sqrt{f_2(\eta)}\, d\eta = n_2 h, \\ \sqrt{m_0}\int_0^{2\pi} \alpha\, d\psi = n_3 h, \end{aligned}\right\} \quad . \quad (1)$$

where h is Planck's quantum of action, $n_1\ n_2\ n_3$ are whole numbers, m_0 is the mass of the electron, and $f_1(\xi)\ f_2(\eta)$ are given by

$$\left.\begin{aligned} \frac{1}{m_0} f_1(\xi) = 2(e\mathrm{E} + \beta) + 2\mathrm{W}\xi^2 - e\mathrm{F}\xi^4 - \frac{\alpha^2}{\xi^2}, \\ \frac{1}{m_0} f_2(\eta) = 2(e\mathrm{E} - \beta) + 2\mathrm{W}\eta^2 + e\mathrm{F}\eta^4 - \frac{\alpha^2}{\eta^2}, \end{aligned}\right\} \quad . \quad (2)$$

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* For the H lines, *e. g.*, Stark used a field of about 28,500 volt × $\mathrm{cm.}^{-1}$ (=95 C.G.S. electrostatic units). We find that a field of about 10 times this strength would give quite measurable effects.

Here $(-e)$ is the charge on the electron, E that on the nucleus, and α, β, W are constants arising from the integration of the Jacobian Differential Equation[*]. W represents the energy of the electron. The coordinates ξ and η are parabolic coordinates in accordance with the equation

$$x+iy=\tfrac{1}{2}(\xi+i\eta)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where x, y, z are Cartesian coordinates at the nucleus, Ox *being chosen parallel to the external field* F. The limits of integration for the two first integrals in (1) are the maxima and minima of ξ and η respectively. Now these two integrals are both of the same form ; so that we can write :

$$\int_0 \sqrt{A+\frac{2B}{r}+\frac{C}{r^2}+Dr}\,dr=2nh, \quad . \quad . \quad . \quad (4)$$

thus denoting the two cases for ξ and η by the suffixes 1 and 2 respectively we have

$$\left.\begin{aligned} A_1&=2m_0W, \quad B_1=m_0(eE+\beta), \quad C_1=-\left(\frac{n_3h}{2\pi}\right)^2, \\ D_1&=-m_0eF\,; \end{aligned}\right\} \quad (5\,a)$$

$$\left.\begin{aligned} A_2&=2m_0W, \quad B_2=m_0(eE-\beta), \quad C_2=-\left(\frac{n_3h}{2\pi}\right)^2, \\ D_2&=+m_0eF. \end{aligned}\right\} \quad (5\,b)$$

Now Sommerfeld[†] works out the value of the contour integral on the left-hand side. The value he gives is

$$2\pi i\left\{\sqrt{C}+\frac{B}{\sqrt{A}}+\frac{D}{4A^{3/2}}\left(\frac{3B^2}{A}-C\right)\right\}. \quad . \quad . \quad (6)$$

From (4) and (6) we can write,

$$B=-\sqrt{A}\left(\sqrt{C}+\frac{nhi}{\pi}\right)+\frac{D}{4A}\left(C-\frac{3B^2}{A}\right). \quad . \quad (7)$$

Both Sommerfeld and Epstein have obtained the value of W [which Epstein denotes by (−A)] by slightly different methods to the first order in F [Epstein's (−E)]. We shall proceed to a second approximation.

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[*] For a fuller treatment of this section, see Epstein's paper already referred to, also Sommerfeld's 'Atombau u.s.w.' II. Auf. p. 542, and p. 482. Jacobi's method of integrating the Hamiltonian transformed equations is also given by Appell, 'Mécanique rationelle,' ii. p. 400 (Paris, 1904).

[†] 'Atombau u.s.w.' Zusatz vii. p. 482, under f.; we, however, write $\sqrt{C}$ for his $(-\sqrt{C})$.

§ 3. *Calculations for Comparatively Large Fields.*

We shall treat the term in D in equation (7) as a corrective term. Let $\overset{0}{\beta}$, $\overset{0}{\beta}+\overset{0}{\Delta}\beta=\beta'$, $\beta'+\Delta'\beta=\beta''$, etc., denote the successive approximations to the value of β; similarly for A, B, and W. We see that to the first order of small quantities

$$\overset{1}{B}_1{}^2=[\overset{0}{B}_1+\overset{0}{\Delta}B_1]^2=[\overset{0}{B}_1+m_0\overset{0}{\Delta}\beta]^2 \quad \text{from } (5\,a)$$

$$\doteq \overset{0}{B}_1{}^2+2m_0\overset{0}{B}_1\overset{0}{\Delta}\beta, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8\,a)$$

and similarly

$$\overset{1}{B}_2{}^2 \doteq \overset{0}{B}_2{}^2-2m_0\overset{0}{B}_2\overset{0}{\Delta}\beta \quad \text{from } (5\,b). \quad . \quad . \quad . \quad (8\,b)$$

Now the equations for determining $\overset{0}{\Delta}\beta$ could easily be solved, but as we are assuming Epstein's work we shall merely give here the value obtained on solving his equations (61) *. We have

$$\overset{0}{\Delta}\beta=\frac{\text{N}\,.\,\text{F}\,.\,h^4(n_1+n_2+n_3)}{64m_0{}^2e\text{E}^2\pi^4}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where

$$\text{N}\equiv(6n_2{}^2+6n_2n_3+n_3{}^2)(2n_1+n_3)$$

$$+(6n_1{}^2+6n_1n_2+n_3{}^2)(2n_2+n_3), \quad (10)$$

so that we have from (8) and (9)

$$\overset{1}{B}_1{}^2=\overset{0}{B}_1{}^2+2m_0\overset{0}{B}_1\times\frac{h^4(n_1+n_2+n_3)\text{N}}{64m_0{}^2e\text{E}^2\pi^4}\text{F}, \quad . \quad (11\,a)$$

similarly

$$\overset{1}{B}_2{}^2=\overset{0}{B}_2{}^2-2m_0\overset{0}{B}_2\times\frac{h^4\,.\,(n_1+n_2+n_3)\,.\,\text{N}}{64m_0{}^2e\text{E}^2\pi^4}\,.\,\text{F}; \quad (11\,b)$$

also, $\overset{0}{B}{}^2$ is obtained from (7) on neglecting the term in D, thus:

$$\overset{0}{B}{}^2=\text{A}\left(\sqrt{\text{C}}+\frac{nhi}{\pi}\right)^2. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

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* *Ann. d. Phys.* l. p. 508 (1916); our $\overset{0}{\Delta}\beta$ corresponds to Epstein's $(e^2\Delta\beta)$.

From (11) and (12) we have

$$\overset{1}{\mathrm{B}}{}^2=\mathrm{A}\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)^2\mp\frac{h^4(n_1+n_2+n_3)\sqrt{\mathrm{A}}\mathrm{N}}{32m_0e\mathrm{E}^2\pi^4}\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)\mathrm{F}. \quad . \quad . \quad . \quad (13)$$

Substituting this value for B² in the term involving D on the right-hand side of (7), we have

$$\mathrm{B}=-\sqrt{\mathrm{A}}\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)+\frac{\mathrm{D}}{4\mathrm{A}}\left\{\mathrm{C}-3\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)^2\right.$$
$$\left.\pm\mathrm{F}\times\frac{3h^4(n_1+n_2+n_3)\mathrm{N}\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)}{32m_0e\mathrm{E}^2\sqrt{\mathrm{A}}\,\pi^4}\right\},$$

or, substituting the values of D from (5), we have

$$\mathrm{B}=-\sqrt{\mathrm{A}}\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)\mp\frac{m_0e}{4\mathrm{A}}\left\{\mathrm{C}-3\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)^2\right\}\mathrm{F}$$
$$-\frac{3h^4(n_1+n_2+n_3)\mathrm{N}\left(\sqrt{\mathrm{C}}+\frac{nhi}{\pi}\right)}{128\mathrm{E}^2\pi^4\mathrm{A}^{3/2}}\mathrm{F}^2; \quad . \quad (14)$$

writing the two equations embodied in (14) in full and adding, we obtain

$$m_0e\mathrm{E}=-\sqrt{\mathrm{A}}\left(\sqrt{\mathrm{C}}+\frac{(n_1+n_2)hi}{2\pi}\right)$$
$$+\frac{m_0e\mathrm{F}}{4\mathrm{A}}\left(\frac{3}{2}\frac{(n_2{}^2-n_1{}^2)h^2}{\pi^2}-\frac{3(n_2-n_1)hi\sqrt{\mathrm{C}}}{\pi}\right)$$
$$-\frac{3h^4(n_1+n_2+n_3)\mathrm{N}}{128\mathrm{A}^{3.2}\pi^4\mathrm{E}^2}\left[\sqrt{\mathrm{C}}+\frac{(n_1+n_2)hi}{2\pi}\right]\mathrm{F}^2. \quad . \quad (15)$$

We proceed to solve for A by putting

$$\mathrm{A}=-(\mathrm{K}+\mathrm{LF}+\mathrm{MF}^2). \quad . \quad . \quad . \quad . \quad (16)$$

We have

$$\left.\begin{aligned}\sqrt{\mathrm{A}}&=i\sqrt{\mathrm{K}}\left(1+\frac{1}{2}\frac{\mathrm{L}}{\mathrm{K}}\mathrm{F}+\frac{1}{8}\frac{4\mathrm{MK}-\mathrm{L}^2}{\mathrm{K}^2}\mathrm{F}^2\right)\\&\qquad\qquad\qquad\text{approximately,}\\\text{and}\quad\frac{1}{\mathrm{A}}&=-\frac{1}{\mathrm{K}}\left(1-\frac{\mathrm{L}}{\mathrm{K}}\mathrm{F}\right)\qquad\qquad\text{,,}\\\text{and}\quad\frac{1}{\mathrm{A}^{3/2}}&=\frac{i}{\mathrm{K}^{3/2}}\qquad\qquad\qquad\quad\text{,,}\end{aligned}\right\}\quad(17)$$

Thus, substituting in (15) and putting

$$\sqrt{C} = \frac{n_3 hi}{2\pi},$$

we have, on equating the coefficients of powers of F,

$$K = +\frac{4\pi^2(m_0 e E)^2}{(n_1+n_2+n_3)^2 h^2}, \quad \ldots \ldots \ldots \quad (18)$$

$$L = \frac{3h^2}{4\pi^2 E}(n_2-n_1)(n_1+n_2+n_3), \quad \ldots \quad (19)$$

$$M = \frac{L^2}{4K} - \frac{3m_0 e h L}{2\pi K^{3/2}}(n_2-n_1) - \frac{3h^4(n_1+n_2+n_3)N}{64\pi^4 E^2 K}. \quad \ldots \quad (20)$$

On substituting from (18) and (19) in (20), we finally obtain

$$M = \frac{-27h^6(n_1+n_2+n_3)^3}{256\pi^6 E^4 m_0^2 e^2} N', \quad \ldots \quad (21)$$

where $$N' = (n_1+n_2+n_3)(n_2-n_1)^2 + N. \quad \ldots \quad (22)$$

We thus finally have the full expression for the energy :

$$W = -\frac{2\pi^2 m_0 e^2 E^2}{(n_1+n_2+n_3)^2 h^2} - \frac{3Fh^2}{8\pi^2 m_0 E}(n_2-n_1)(n_1+n_2+n_3) + \frac{27h^6(n_1+n_2+n_3)^3}{512\pi^6 E^4 m_0^3 e^2} N'F^2. \quad \ldots \quad (23)$$

Thus if ΔW represent the change in W due to the introduction of the external field F, we have

$$-\Delta W = \frac{3Fh^2}{8\pi^2 m_0 E}(n_2-n_1)(n_1+n_2+n_3) - \frac{27h^6(n_1+n_2+n_3)^3}{512\pi^6 E^4 m_0^3 e^2} N'F^2. \quad \ldots \quad (24)$$

Thus $\Delta\nu$ [the corresponding change in frequency] is given, according to Bohr's assumption

$$h\Delta\nu = \Delta W_m - \Delta W_n,$$

where W_m denotes the energy for motion in a path [characterized by the quantum numbers $m_1\, m_2\, m_3$] from which the electron starts to move towards the n-path, by the formula

$$\Delta\nu = \frac{3hF}{8\pi^2 m_0 E}\{(n_2-n_1)(n_1+n_2+n_3) - (m_2-m_1)(m_1+m_2+m_3)\} + \frac{27h^5F^2}{512\pi^6 E^4 m_0^3 e^2} - (n_1+n_2+n_3)^3 N'(n) + (m_1+m_2+m_3)N'(m)\}, \quad . \quad (25)$$

where $N'(m)$ and $N'(n)$ are identical functions of m and n respectively.

§ 4. *Application to the* H_α *line.*

We proceed to apply equation (25) to specific lines of the elements. Let us take as an example the H_α line of the Balmer Series. Here $n_1+n_2+n_3=2$, $m_1+m_2+m_3=3$, $\nu=4{\cdot}571\times10^{14}$, $\lambda={\cdot}65628\times10^{-4}$; let us also write (25) in the form

$$\Delta\nu=(P_1-Q_1)\times K_1F+(Q_2-P_2)K_2F^2\,; \qquad (26)$$

then

$$\left.\begin{aligned}
&P_1=(n_2-n_1)(n_1+n_2+n_3),\quad Q_1=(m_2-m_1)(m_1+m_2+m_3),\\
&\qquad K_1=\frac{3h}{8\pi^2m_0E},\\
&P_2=(n_1+n_2+n_3)^4(n_2-n_1)^2+(n_1+n_2+n_3)^3N(n),\\
&Q_2=(m_1+m_2+m_3)^4(m_2-m_1)^2+(m_1+m_2+m_3)^3N(m),\\
&\qquad K_2=\frac{27h^5}{512\pi^6E^4m_0{}^3e^2},
\end{aligned}\right\} \qquad (27)$$

Then writing down in a tabular form the possible values of $n_1\,n_2\,n_3$ and $m_1\,m_2\,m_3$, we have, on availing ourselves of Sommerfeld's "Auswahlprinzip" for the definition of the plane of polarization and the restrictions on the possible combinations of the quantum numbers:

TABLE A.

	n_3.	n_2.	n_1.	P_1.	P_2.		m_3.	m_2.	m_1.	Q_1.	Q_2.
I.	2	0	0	0	128	*a*.	3	0	0	0	1458
II.	1	1	0	2	144	*b*.	2	1	0	3	2025
III.	1	0	1	−2	144	*c*.	2	0	1	−3	2025
IV.	0	1	1	0	192	*d*.	1	1	1	0	2106
V.	0	2	0	4	64	*e*.	1	2	0	6	1458
VI.	0	0	2	−4	64	*f*.	1	0	2	−6	1458
						g.	0	2	1	3	2025
						h.	0	1	2	−3	2025
						i.	0	3	0	9	729
						j.	0	0	3	−9	729

TABLE B.

First Group. $m_3-n_3=0$; p-component.

	P_1-Q_1.	Q_2-P_2.		P_1-Q_1.	Q_2-P_2.
(I. *b*)	− 3	1897	(I. *c*)	+ 3	1897
(II. *d*)	+ 2	1962	(III. *d*) ...	− 2	1962
(II. *e*)	− 4	1314	(III. *f*) ...	+ 4	1314
(II. *f*)	+ 8	1314	(III. *e*)......	− 8	1314
(IV. *g*)......	− 3	1833	(IV. *h*) ...	+ 3	1833
(IV. *i*)	− 9	537	(IV. *j*) ...	+ 9	537
(V. *g*)	+ 1	1951	(VI. *h*) ...	− 1	1951
(V. *h*)	+ 7	1951	(VI. *g*) ...	− 7	1951
(V. *i*)	− 5	665	(VI. *g*) ...	+ 5	665
(V. *j*)	+13	665	(VI. *i*) ...	−13	665

TABLE C.

Second Group. $m_3-n_3=\pm 1$; n-component.

	P_1-Q_1.	Q_2-P_2.		P_1-Q_1.	Q_2-P_2.
(I. *a*)	0	1330	(I. *d*)	0	1978
(I. *e*)	− 6	1330	(I. *f*)	+ 6	1330
(II. *b*)	− 1	1881	(III. *c*) ...	+ 1	1881
(II. *c*)	+ 5	1881	(III. *b*) ...	− 5	1881
(II. *g*)	− 1	1881	(III. *h*) ...	+ 1	1881
(II. *h*)	+ 5	1881	(III. *g*) ...	− 5	1881
(II. *i*)	− 7	589	(III. *j*) ...	+ 7	589
(II. *j*)	+11	589	(III. *i*) ...	−11	589
(IV. *e*)......	− 6	1266	(IV. *f*) ...	+ 6	1266
(V. *e*)	− 2	1394	(VI. *f*) ...	+ 2	1394
(V. *f*)	+10	1394	(VI. *e*) ...	−10	1394
(V. *d*)	+ 4	2042	(VI. *d*) ...	− 4	2042
(IV. *d*)......	0	1914			

The arrangement of the tables is very simple. In Table A we put down all the possible values for the n's and the m's separately for the line H_α. Then in Tables B and C we choose such combinations as give rise to $m_3 - n_3 = 0$ or $m_3 - n_3 = \pm 1$ respectively. The group in Table A corresponds to lines where the plane of polarization is perpendicular to the impressed field F [*i. e.* the electric force parallel to F], and that of Table B to lines where the light is polarized in a plane parallel to F [*i. e.* the electric force perpendicular to F].

We observe that whereas $(P_1 - Q_1)$ has a negative value numerically equal to every one of its possible positive values, $(Q_2 - P_2)$ *on the other hand has an invariable positive sign and a roughly constant order of magnitude, viz.* 10^3.

If we avail ourselves of the most recent values * for the constants involved in the formula (25), viz.

$$h = 6{\cdot}547 \times 10^{-27}, \quad e = 4{\cdot}774 \times 10^{-10}, \quad \frac{e}{m_0} = 5{\cdot}301 \times 10^{17},$$

and if we put $E = e$ for hydrogen, we have

$$K_1 = 5{\cdot}784 \times 10^8. \quad K_2 = 7{\cdot}677 \times 10\,; \quad . \quad . \quad . \qquad (28)$$

so that (26) can now be written

$$\Delta\nu = 5{\cdot}784 \times 10^8 \times Z \times F + 7{\cdot}677 \times R_z \times 10^4 \times F^2, \qquad (29)$$

where

$$Z \equiv (P_1 - Q_1), \quad R_z = \frac{Q_2 - P_2}{1000},$$

or on the scale of wave-lengths, since $\Delta\nu = -\frac{c}{\lambda^2}\,d\lambda$,

$$-\Delta\lambda = {\cdot}8304 \times 10^{-10} \times F \times Z + 1{\cdot}102 \times 10^{-14} \times R_z F^2. \quad (30)$$

Here it must be remembered that F is measured in absolute C.G.S. electrostatic units. In (30) we observe that Z is a whole number, positive or negative, between 0 and 13 and that R_z varies from about $\frac{1}{2}$ to about 2.

If we assume a value for $F = 10^3$ [$= 300{,}000$ volt × cm.$^{-1}$], then if λ' be written for $\lambda \times 10^8$ [*i. e.* if we measure λ', the wave-length, in Ångström units] we write :

$$-\Delta\lambda' = 8{\cdot}304 Z + 1{\cdot}102 \times R_z. \quad . \quad . \quad . \quad . \qquad (31)$$

We thus see that for small values of Z, the second term on the right-hand side of (31) is quite appreciable compared with the first term [*e. g.* for $Z = 1$ the ratio is about $\frac{1}{4}$] ; *and*

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* These are quoted from R. A. Millikan's 'The Electron,' The University of Chicago Press, Third Impression 1918, pp. 238 and 251.

since this term has an invariable value for equal and opposite values of Z, it follows that the symmetry of the lines is destroyed. Also the parabolic relation between $\Delta\nu$ and F [or $\Delta\lambda$ and F] is furnished by (29) and (30) respectively. We give here a table of the displacements of the nine lines observed by Stark for a hypothetical field of 300,000 volt × cm.$^{-1}$ as predicted by our theory.

	p-component.						*n*-component.				
Z ……	+2	−2	+3	−3	+4	−4	0			+1	−1
R_z …	1·962	1·962	1·833	1·833	1·314	1·314	1·978	1·914	1·330	1·881	1·881
$\Delta\lambda'$ …	−18·8	−14·4	−26·9	+22·9	−34·7	+31·8	−2·2	−2·1	−1·5	−10·3	+6·4

The *n*-component line which occupies the original position of the H_α line is seen to split into three components—two of which are, however, very close together—for higher fields. The position of these lines may, however, be appreciably affected by higher terms in equation (30) than the last term we have taken account of (*i. e.* terms in F^3 etc.). It is to be observed that the functions of the quantum numbers involved seem to become more and more important in determining the order of magnitude of the respective terms as we proceed to consider higher powers of F. However, the above calculations ought to furnish a fairly accurate theory for fields of the magnitude we have considered; and, in our opinion, it would be highly desirable to make exact measurements for such fields. Whether the above predictions will or will not be verified, remains to be seen.

In conclusion, I wish to express my thanks to Prof. J. W. Nicholson for useful suggestions.

King's College, London,
May 1921.

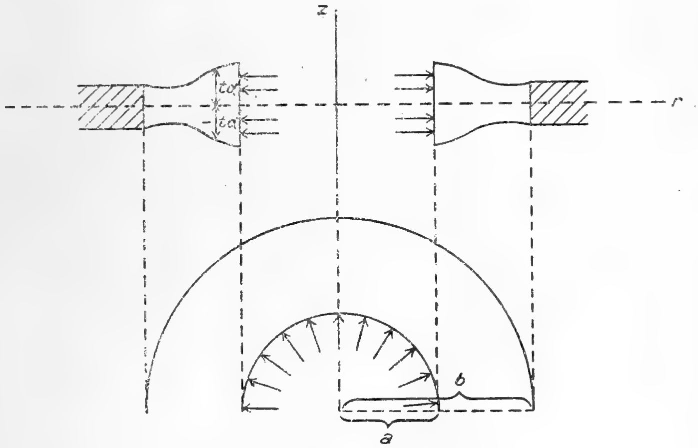
CI. *Circular Plates of Variable Thickness.* *By* George D. Birkhoff, *Ph.D., Professor of Mathematics, Harvard University* [*].

As far as I am aware, only plates and shells of constant thickness have been considered in the theory of elasticity. The aim of the present note is to develop a method applicable when the thickness is variable [†]. The method is here applied to thin circular plates, nearly plane, and clamped at the outer edge.

Case I.—The Incomplete Symmetrical Plate under Radial Pressure.

Suppose that ordinary cylindrical coordinates (fig. 1) are adopted, with the axis of z along the axis of the plate.

Fig. 1.



The plate is of inner radius a and outer radius b, and is symmetrical about the plane $z=0$. Let α be proportional to the thickness of the plate, so that $z=t\alpha$ and $z=-t\alpha$ may be taken as the equations of the upper and lower bases respectively. Here t is a small parameter, since the plate is thin.

Radial forces are applied to the inner edge, so that points

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[*] Communicated by the Author.

[†] I am greatly indebted to Mr. Carl A. Garabedian, of Harvard University, for able assistance in carrying through some of the calculations and for verifying those I have made. Mr. Garabedian is undertaking the consideration of more general problems by this method.

for which $r=a$ undergo a displacement of amount ϵ. The plate is clamped at the outer edge. Thus, if U and w denote the radial and axial displacements, the boundary conditions are

$$\left\{\begin{aligned} &\mathrm{U}(a,0)=\epsilon, \quad \mathrm{U}(b,0)=0, \\ &w(b,0)=\frac{\partial w(b,0)}{\partial r}=0. \end{aligned}\right.$$

Obviously such a plate is unstable, with a tendency to buckle.

It is a cardinal fact of the theory of elasticity that the actual displacement of the plate will be such as to yield the minimum potential energy consistent with the constraints imposed (Love, 'Theory of Elasticity,' third edition, p. 169).

By Love (pp. 99–100, 141) this potential energy W is given as follows:—

$$\mathrm{W}=\pi\int_a^b\int_{-t\alpha}^{t\alpha}\left\{(\lambda+2\mu)\left[\frac{\partial\mathrm{U}}{\partial r}+\frac{\mathrm{U}}{r}+\frac{\partial w}{\partial z}\right]^2\right.$$
$$\left.+\mu\left[\left(\frac{\partial\mathrm{U}}{\partial z}+\frac{\partial w}{\partial r}\right)^2-4\frac{\mathrm{U}}{r}\frac{\partial\mathrm{U}}{\partial r}-4\frac{\mathrm{U}}{r}\frac{\partial w}{\partial z}-4\frac{\partial\mathrm{U}}{\partial r}\frac{\partial w}{\partial z}\right]\right\}r\,dz\,dr.$$

It is natural to introduce a new variable z', such that $z=tz'$. When we replace z by z' and afterward suppress the accents there results:—

$$\text{(A)} \qquad \mathrm{W}=\pi t\int_a^b\int_{-\alpha}^{\alpha}\left\{(\lambda+2\mu)\left[\frac{\partial\mathrm{U}}{\partial r}+\frac{\mathrm{U}}{r}+\frac{1}{t}\frac{\partial w}{\partial z}\right]^2\right.$$
$$\left.+\mu\left[\left(\frac{1}{t}\frac{\partial\mathrm{U}}{\partial z}+\frac{\partial w}{\partial r}\right)^2-4\frac{\mathrm{U}}{r}\frac{\partial\mathrm{U}}{\partial r}-\frac{4}{t}\frac{\mathrm{U}}{r}\frac{\partial w}{\partial z}-\frac{4}{t}\frac{\partial\mathrm{U}}{\partial r}\frac{\partial w}{\partial z}\right]\right\}r\,dz\,dr.$$

Our *assumption* will be that all of the quantities involved can be expanded in ascending powers of t—in particular that

$$\mathrm{U}=\mathrm{U}_0+\mathrm{U}_1t+\mathrm{U}_2t^2+\ldots\ldots,$$
$$w=w_0+w_1t+w_2t^2+\ldots\ldots$$

It is to be noted that if in (A) we replace z by $-z$ and w by $-w$, or t by $-t$ and w by $-w$, the double integral is altered at most in sign. Since these transformations do not disturb our boundary conditions, and since W has a unique minimum, the special relations

$$\text{(B)} \quad \mathrm{U}_m(r,z)-\mathrm{U}_m(r,-z)=w_m(r,z)+w_m(r,-z)=0, \quad m=0,1,2,\ldots,$$

$$\text{(B}'\text{)} \quad \mathrm{U}_{2m+1}(r,z)=w_{2m}(r,z)=0, \quad m=0,1,2,\ldots\ldots,$$

must obtain.

The case of a plane plate shows that the energy is of order t. Hence if W is to be a minimum, it is clear that we must make the leading term of W, namely

$$\frac{\pi\mu}{t}\int_a^b\int_{-\alpha}^{\alpha}\left[\frac{\partial \mathrm{U}_0}{\partial z}\right]^2 r\,dz\,dr,$$

vanish if possible. But this quantity vanishes if, and only if, $\mathrm{U}_0=\mathrm{U}_0(r)$, and by thus restricting U_0 the stated boundary conditions are not violated.

When U_0 is thus restricted, the double integral W will involve no negative powers of t, and will have as leading term :—

$$\pi t\int_a^b\int_{-\alpha}^{\alpha}\left\{(\lambda+2\mu)\left[\mathrm{U}_0'+\frac{\mathrm{U}_0}{r}+\frac{\partial w_1}{\partial z}\right]^2 -4\mu\left[\frac{\mathrm{U}_0}{r}\mathrm{U}_0'+\frac{\mathrm{U}_0}{r}\frac{\partial w_1}{\partial z}+\mathrm{U}_0'\frac{\partial w_1}{\partial z}\right]\right\}r\,dz\,dr,$$

where accents denote differentiation with respect to r. The part of the integrand in braces may be written as the sum of squares :—

$$\lambda\left[\mathrm{U}_0'+\frac{\mathrm{U}_0}{r}+\frac{\partial w_1}{\partial z}\right]^2+2\mu\left[\mathrm{U}_0'^2+\frac{\mathrm{U}_0^2}{r^2}+\left(\frac{\partial w_1}{\partial z}\right)^2\right].$$

We turn next to the choice of $\frac{\partial w_1}{\partial z}$, which is an arbitrary function of r and z still at our disposal. If we call this variable x, the above expression involves x in two terms of the form

$$\lambda(m+x)^2+2\mu x^2.$$

Elementary calculation shows that for $x=\frac{-\lambda m}{\lambda+2\mu}$, the foregoing expression has the minimum value $\frac{2\lambda\mu}{\lambda+2\mu}m^2$. Hence we must take

$$\frac{\partial w_1}{\partial z}=\frac{-\lambda}{\lambda+2\mu}\left(\mathrm{U}_0'+\frac{\mathrm{U}_0}{r}\right),$$

or

$$w_1=\frac{-\lambda z}{\lambda+2\mu}\left(\mathrm{U}_0'+\frac{\mathrm{U}_0}{r}\right)+s(r),$$

$s(r)$ arbitrary. But $w(r,\ 0)=0$ by (B) ; hence $s(r)=0$. This choice of w_1 does not interfere with the boundary conditions.

The terms written above now reduce to give

$$\pi t\int_a^b\int_{-\alpha}^{\alpha}\frac{4\mu}{\lambda+2\mu}\left\{(\lambda+\mu)\left(\mathrm{U}_0'^2+\frac{\mathrm{U}_0^2}{r^2}\right)+\lambda\mathrm{U}_0'\frac{\mathrm{U}_0}{r}\right\}r\,dz\,dr,$$

and an integration with regard to z can be explicitly performed. The principal part of W takes the form $W_1 t$, where

$$W_1=\frac{8\pi\mu}{\lambda+2\mu}\int_a^b\left\{(\lambda+\mu)\left(U_0'^2+\frac{U_0^2}{r^2}\right)+\lambda U_0'\frac{U_0}{r}\right\}\alpha r\,dr. \qquad (1)$$

This integral is to be made a minimum subject to the boundary conditions

$$U_0(a)=\epsilon, \quad U_0(b)=0.$$

Accordingly our problem is reduced to a simple problem in the Calculus of Variations. The condition $\delta W_1=0$ gives at once

$$\frac{d}{dr}\frac{\partial\Phi}{\partial U_0'}-\frac{\partial\Phi}{\partial U_0}=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where Φ is the integrand in (1). Writing out this equation in full, we obtain

$$\frac{d}{dr}\left[2(\lambda+\mu)U_0'+\lambda\frac{U_0}{r}\right]\alpha r-\left[2(\lambda+\mu)\frac{U_0}{r}+\lambda U_0'\right]\alpha=0.$$

Consequently U_0 must satisfy the folllowing differential equation :—

$$U_0''+\frac{U_0'}{r}-\frac{U_0}{r^2}=-\frac{h'}{h}\left(U_0'+\frac{\lambda}{2(\lambda+\mu)}\frac{U_0}{r}\right), \quad . \quad (3)$$

where $2h=2t\alpha$ stands for the thickness of the plate.

In the case of a plate of constant thickness, h is constant and $h'=0$, and (3) reduces to a well-known form (Love, p. 141).

Thus far we have determined the displacements to be

$$U=U_0(r)+U_2t^2+\ldots\ldots, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$w=-\frac{\lambda z}{\lambda+2\mu}\left(U_0'+\frac{U_0}{r}\right)t+w_3t^3+\ldots\ldots, \quad . \quad (5$$

where it is to be remembered that the accent on z has been suppressed.

We proceed to determine U_2 from the fact that the body forces F_r, F_z must vanish. We have (Love, p. 141) :

$$-\rho F_r=(\lambda+2\mu)\left(U''+\frac{U'}{r}-\frac{U}{r^2}\right)+\frac{\lambda+\mu}{t}\frac{\partial w}{\partial z\partial r}+\frac{\mu}{t^2}\frac{\partial^2 U}{\partial z^2}=0,$$
$$. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$-\rho F_z=\frac{\lambda+2\mu}{t^2}\frac{\partial^2 w}{\partial z^2}+\frac{\lambda+\mu}{t}\frac{\partial}{\partial z}\left(U'+\frac{U}{r}\right)$$
$$+\mu\left(\frac{1}{r}\frac{\partial w}{\partial r}+\frac{\partial^2 w}{\partial r^2}\right)=0. \quad . \quad (7)$$

Substituting (4) and (5) in (6) and (7), the terms in t^{-2} and t^{-1} vanish. From the constant term in (6) we obtain

$$\frac{\partial^2 U_2}{\partial z^2} = -\frac{3\lambda+4\mu}{\lambda+2\mu}\left(U_0'' + \frac{U_0'}{r} - \frac{U_0}{r^2}\right),$$

whence, using (B),

$$U_2 = -\frac{3\lambda+4\mu}{2(\lambda+2\mu)}\, z^2\left(U_0'' + \frac{U_0'}{r} - \frac{U_0}{r^2}\right) + g(r).$$

Also, the constant term in (7) vanishes.

Furthermore, the surface tractions must vanish on the free surfaces $z=\alpha$, $z=-\alpha$; hence (Love, p. 76) the following equations must hold on these surfaces :—

$$\left.\begin{aligned} X_\nu &= X_x \cos(x,\nu) + X_y \cos(y,\nu) + X_z \cos(z,\nu) = 0, \\ Y_\nu &= Y_x \cos(x,\nu) + Y_y \cos(y,\nu) + Y_z \cos(z,\nu) = 0, \\ Z_\nu &= Z_x \cos(x,\nu) + Z_y \cos(y,\nu) + Z_z \cos(z,\nu) = 0. \end{aligned}\right\} \quad (8)$$

If we consider a tangent plane at an arbitrary point of the surface $z=\alpha$, the direction of the normal is denoted by ν, and (8) gives the tractions across the tangent plane in terms of the stress-components across planes parallel to the rectangular coordinate planes. For cylindrical coordinates, we have (Love, pp. 100, 141) :—

$$X_x = \lambda\Delta + 2\mu e_{xx} = \lambda\Delta + 2\mu\frac{\partial U}{\partial r},$$

$$Y_y = \lambda\Delta + 2\mu e_{yy} = \lambda\Delta + 2\mu\frac{U}{r},$$

$$Z_z = \lambda\Delta + 2\mu e_{zz} = \lambda\Delta + 2\mu\frac{1}{t}\frac{\partial w}{\partial z},$$

$$Y_z = Z_y = \mu e_{yz} = 0,$$

$$Z_x = X_z = \mu e_{zx} = \mu\left(\frac{1}{t}\frac{\partial U}{\partial z} + \frac{\partial w}{\partial r}\right),$$

$$X_y = Y_x = \mu e_{xy} = 0,$$

where

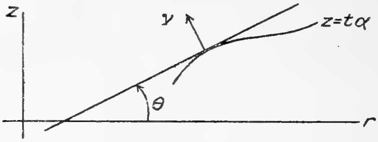
$$\Delta = U' + \frac{U}{r} + \frac{1}{t}\frac{\partial w}{\partial z}.$$

To determine the direction cosines, we return to our original variables and observe that $\tan\theta = t\alpha'$.

Hence we find along the x axis

$$\cos(x,\nu)=\frac{-t\alpha'}{\sqrt{1+t^2\alpha'^2}},\quad \cos(y,\nu)=0,\quad \cos(z,\nu)=\frac{1}{\sqrt{1+t^2\alpha'^2}}.$$

Fig. 2.



Hence the conditions that the tractions vanish on the free surfaces become

$$-t\alpha' X_x + X_z = 0, \quad \ldots\ldots \quad (9)$$

$$-t\alpha' Z_x + Z_z = 0. \quad \ldots\ldots \quad (10)$$

As we proceed to higher order terms, using (6) and (7), the relations (9) and (10) may be expected to play an important rôle in furnishing differential equations to determine the arbitrary functions that enter. In the present case there is no constant term in either left-hand member; and by virtue of (3) the terms in t also vanish.

Thus the surplus body forces per unit of volume vanish up to order t, and the surplus surface tractions per unit of area vanish up to order t^2. Hence the total surplus applied force is of the order t^2, whereas the total given radial force is of order t. It seems clear that when the surplus applied forces are removed, no sensible change occurs in the radial or axial displacement, and that we have a solution of our problem.

It remains to compute the principal part of the radial pressure on the inner edge of the plate. Here we make use of Saint Venant's principle and obtain the resultant traction, $X_x(r, z)$, as

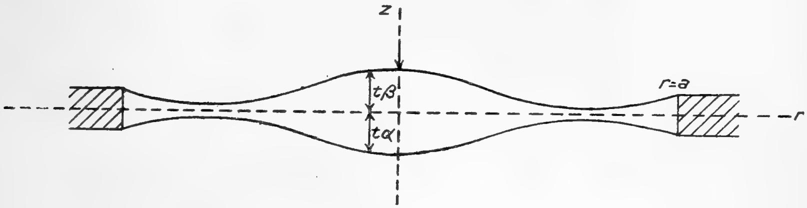
$$\int_0^{2\pi}\int_{-t\alpha(a)}^{t\alpha(a)} X_x(a,0)\,a\,dr\,d\theta = \frac{8\pi a\mu(\lambda+\mu)h(a)}{\lambda+2\mu}\left[U_0'(a)+\frac{\lambda}{2(\lambda+\mu)}\frac{U_0(a)}{a}\right].$$

If we desire to take $t=1$ throughout, so that the equations of the bases are $z=\alpha$ and $z=-\alpha$, then t disappears as an explicit parameter, but the terms of the solution are still ordered according to the powers of the natural parameter, namely the ratio of the thickness of the plate to its diameter.

Case II.—The Complete Plate under Axial Pressure.

As a second example consider a thin circular plate, nearly plane, clamped at the outer edge and subject to an axial force P. Here a small force P yields a relatively large displacement, and our method is put to a more delicate test. Again adopt cylindrical coordinates (fig. 3).

Fig. 3.



The plate is not restricted to be symmetrical. Accordingly let α and β be proportional to the distances of the bases of the plate from the plane $z=0$, so that $z=t\alpha$ and $z=t\beta$ are the equations of the lower and upper bases respectively.

The boundary conditions are the following :—

$$\left\{\begin{array}{l} U(0,\,0)=0, \quad w(0,\,0)=\epsilon, \\ w(a,\,0)=\dfrac{\partial w(a,\,0)}{\partial r}=0. \end{array}\right.$$

Again, we take the formula for potential energy as the point of departure. The term in t^{-1} is now

$$\frac{\pi}{t}\int_0^a\int_\alpha^\beta \left\{ (\lambda+2\mu)\left[\frac{\partial w_0}{\partial z}\right]^2+\mu\left[\frac{\partial U_0}{\partial z}\right]^2\right\} r\,dz\,dr.$$

This term can only be made to vanish by setting

$$w_0=w_0(r), \quad U_0=U_0(r),$$

and the boundary conditions are not thereby violated.

The constant term in W disappears and we can write the integrand of the term in t as the sum of squares :—

$$\left[U_0'+\frac{U_0}{r}+\frac{\partial w_1}{\partial z}\right]^2+2\mu\left[U_0'^2+\frac{U_0^2}{r^2}+\left(\frac{\partial w_1}{\partial z}\right)^2\right] \\ +\mu\left[\frac{\partial U_1}{\partial z}+w_0'\right]^2.$$

In the present case we are led to attempt to make this integrand vanish, since the case of an ordinary plane plate shows that the energy will be of order t^3. Thus we must take

$$U_0=0, \quad w_1=w_1(r), \quad U_1=-zw_0'+p(r),$$

where $p(r)$ is arbitrary. None of these requirements violate the boundary conditions.

The physical significance of the conditions thus far obtained is immediate; the displacement is transverse, and such that filaments perpendicular to $z=0$ remain perpendicular in the displaced position and are not compressed transversely.

When these conditions are imposed, it is easy to see that the energy is of the order t^3. More precisely, the leading term in W now becomes

$$\pi t^3\int_0^a\int_\alpha^\beta \Big\{(\lambda+2\mu)\Big[-zw_0''+p'+\frac{-zw_0'+p}{r}+\frac{\partial w_2}{\partial z}\Big]^2$$
$$+\mu\Big[\Big(\frac{\partial U_2}{\partial z}+w_1'\Big)^2-4\Big(\frac{-zw_0'+p}{r}\Big)(-zw_0''+p')$$
$$-4\Big[\Big(\frac{-zw_0'+p}{r}\Big)\frac{\partial w_2}{\partial z}-4(-zw_0''+p')\frac{\partial w_2}{\partial z}\Big]\Big\}\,r\,dz\,dr.$$

The part of the integrand in braces may be written as

$$\lambda\Big[-zw_0''+p'+\frac{-zw_0'+p}{r}+\frac{\partial w_2}{\partial z}\Big]^2$$
$$+2\mu\Big[(-zw_0''+p')^2+\frac{1}{r^2}(-zw_0'+p)^2+\Big(\frac{\partial w_2}{\partial z}\Big)^2\Big]$$
$$+\mu\Big[\frac{\partial U_2}{\partial z}+w_1'\Big]^2.$$

Since U_2 appears only in the last term, and since W is to be a minimum, we choose

$$U_2=-zw_1'+q(r).$$

We proceed next to the choice of $\frac{\partial w_2}{\partial z}$, and find (by the same method as employed in the first example):—

$$\frac{\partial w_2}{\partial z}=\frac{-\lambda}{\lambda+2\mu}\Big(-zw_0''+p'+\frac{-zw_0'+p}{r}\Big),$$

$$w_2=\frac{\lambda}{\lambda+2\mu}\left[\frac{z^2}{2}w_0''-zp'+\frac{\frac{z^2}{2}w_0'-zp}{r}+s(r)\right],$$

$s(r)$ arbitrary. It may be noted that the choice of U_2, w_2 does not interfere with the boundary conditions.

The integral written above thus becomes

$$\pi t^3\int_0^a\int_\alpha^\beta\left\{\frac{4\mu}{\lambda+2\mu}\left[(\lambda+2\mu)\left\{(-zw_0''+p')^2+\frac{1}{r^2}(-zw_0'+p)^2\right\}\right.\right.$$
$$\left.\left.+\lambda(-zw_0''+p')\left(\frac{-zw_0'+p}{r}\right)\right]\right\}r\,dr\,dz,$$

and an integration with regard to z can be explicitly performed. To this end it is convenient to introduce a new variable z', where

$$z=m+z',\quad \beta=m+h,\quad \alpha=m-h;$$

at the same time we replace p by v, where

$$hv=-mw_0'+p,$$

so that hvt is the radial displacement for the mean surface $z=m$. With this notation the principal part W_3t^3 of W has a coefficient.

$$W_3=\frac{8\pi\mu}{\lambda+2\mu}\int_0^a\left\{(\lambda+\mu)\left[\frac{w_0''^2}{3}+\frac{1}{3r^2}w_0'^2\right.\right.$$
$$\left.+\left(v'+\frac{h'}{h}v+\frac{m'}{h}w_0'\right)^2+\frac{v^2}{r^2}\right]$$
$$\left.+\lambda\left[\frac{w_0'w_0''}{3r}+\frac{v}{r}\left(v'+\frac{h'}{h}v+\frac{m'}{h}w_0'\right)\right]\right\}h^3r\,dr. \quad . \quad . \quad (11)$$

It is to be observed that $\frac{h'}{h}$, $\frac{m'}{h}$ are independent of the thickness of the plate.

The integral is to be made a minimum subject to the boundary conditions

$$\left.\begin{array}{r}w_0(0)=\epsilon,\quad w_0(a)=0,\quad w_0'(a)=0;\\ v(0)=v(a)=0.\end{array}\right\} \quad . \quad . \quad . \quad (12)$$

The form of W shows that $w_0'(0)$ vanishes also; otherwise the integral would be infinite.

Our problem is now one in the Calculus of Variations, and the condition $\delta W_3=0$ gives us

$$\frac{d}{dr}\frac{\partial\Phi}{\partial w_0''}-\frac{\partial\Phi}{\partial w_0'}=0,\quad \frac{d}{dr}\frac{\partial\Phi}{\partial v'}-\frac{\partial\Phi}{\partial v}=0, \quad . \quad (13)$$

where Φ is the integrand in (11). We will not write out these equations. The system of two equations is of the fifth order. The five arbitrary constants in the general solution are determined by (12). One of these is an additive constant in w_0, since w_0 does not occur explicitly.

For the case of a *symmetrical* plate we have $m'=0$, and the variables separate. The equations assume the simpler form :—

$$\frac{d}{dr}\left[h^3r\left\{2(\lambda+\mu)\frac{w_0''}{3}+\frac{\lambda w_0'}{3r}\right\}\right]-h^3r\left\{2(\lambda+\mu)\frac{w_0'}{3r^2}+\frac{\lambda w_0''}{3r}\right\}=0,$$

$$\frac{d}{dr}\left[h^3r\left\{2(\lambda+\mu)(v'+\frac{h'}{h}v)+\frac{\lambda v}{r}\right\}\right]-h^3r\left\{2(\lambda+\mu)\frac{h'}{h}\left(v'+\frac{h'}{h}v\right)\right.$$
$$\left.+2(\lambda+\mu)\frac{v}{r^2}+\frac{\lambda}{r}\left(v'+2\frac{h'}{h}v\right)\right\}+0.$$

If, furthermore, the plate is of constant thickness, the equations in w_0' and v become the same :—

$$r^2v''+rv'-v=0, \quad r^2w_0'''+rw_0''-w_0'=0.$$

This differential equation for w_0 coincides with that obtained in the usual theory (Love, p. 494).

When w_0 and v have been determined in the general case, the displacements are given by the formulas :—

$$\mathrm{U}=-(z-m)w_0't+hvt+\ldots\ldots,$$

$$w=w_0+w_1t+\frac{\lambda}{\lambda+2\mu}\left[\frac{z^2}{2}\left(w_0''+\frac{w_0'}{r}\right)-z\left\{\frac{d}{dr}\left(mw_0'+hv\right)\right.\right.$$
$$\left.\left.+\frac{mw_0'+hv}{r}\right\}\right]t^2+\ldots$$

It seems possible to proceed with this example, as in the earlier case, by considering the body forces and surface tractions, and determining terms in U and w of higher order.

The problem of the thin circular plate under special conditions has thus been formally treated by means of the following method, apparently applicable to thin plates, shells, and beams :—(1) introduction of a small parameter t to represent distance from a fundamental mean surface or line ; (2) expansion of the Lagrangian function T—U, the displacements, the body forces, and the surface tractions as power series in t ; (3) determination of the early coefficients so as to make this integral a minimum of as high order as possible in t ; and (4) determination of later coefficients so that the body forces and surface tractions have the required values.

CII. *The Effective Capacity of Multilayer Coils with Square and Circular Section.* By GREGORY BREIT, *Ph.D.*[*]

IT has been shown in a previous paper[†] that the effective capacity of a coil can be computed as

$$C_0 = \int_{x_1}^{x_2} \frac{M(x)}{L} \left\{ \int_{x_1}^{x} \frac{\alpha(x)}{L}\, dx \right\} dx,$$

where

x is an arbitrary parameter along the wire,

L is the inductance of the coil,

$M(x)dx$ is the mutual inductance of the section between x and $x+dx$ to the rest of the coil,

$\left(\frac{di}{dt}\right)\alpha(x)dx$ is the charge on the element dx, i being the current through the coil terminal,

x_1, x_2 are the values of x at the terminals of the coil, the value x_1 corresponding to the ungrounded terminal of the coil.

In the paper mentioned, the formula has been applied to short single-layer solenoids. In this paper the same formula will be applied to two types of multilayer coils having a large diameter. To be specific, consider a multilayer coil having a circular cross section. A section of such a coil by a plane through its axis is shown in fig. 1. Here AB is the axis. The circles FGH, F′G′H′ represent the cross section of the coil. The centres of these cross sections are represented by O and O′. The radius of either of the circles FGH, F′G′H′ is denoted by a. The radius of the circle through O and O′ and having its centre at D (the point of intersection of AB and OO′) is denoted by $\frac{l}{2\pi}$. Thus the circumference of the circle last mentioned is l.

It has been assumed that l is large compared with a. Thus (see G. Breit, *loc. cit.*) the flux through one turn of the coil is the same as that through any other. If, therefore, the manner in which the layers of the coil are arranged is known, then the relative potential of the various parts of the coil is known.

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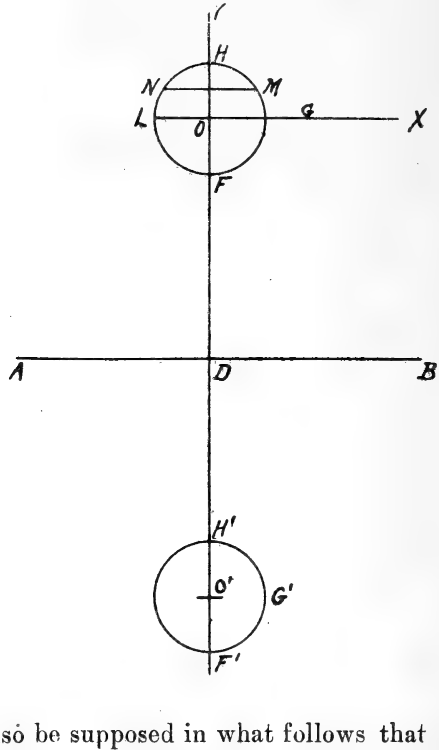
[*] Communicated by the Director of the Bureau of Standards, Washington.

[†] G. Breit, "The Distributed Capacity of Inductance Coils," Phys. Rev. xvii. pp. 649–677 (June 1921).

The coil is supposed to be wound in regular layers, the spacing of the wires in each layer being the same and the spacing of one layer from another being also the same for all layers but not necessarily the same as the spacing of the wires in each layer. This is shown in fig. 2, where h_1 is the spacing of the wires in one layer, and h_2 the spacing between two adjacent layers.

Fig. 1.—Section of coil with circular cross section.



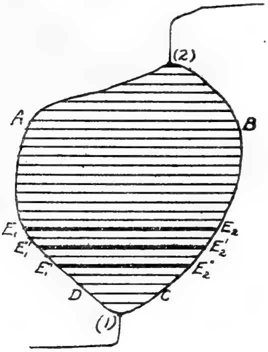
It will also be supposed in what follows that the number of turns in each layer is so large that the potential drop in any one of them is negligible in comparison with the whole potential drop in the layer. It is further assumed that the number of layers is so large that the potential drop in any one layer is only a small fraction of the potential drop in the whole coil.

These assumptions are clearly realized in practice only if very thin wire is employed in winding the coil.

Under the conditions mentioned above, it is immaterial whether the right end of the layer I (see fig. 2) is joined directly to the right or to the left end of the layer II. It is essential, however, for the treatment here given to connect the layers consecutively—*i. e.*, to make the layer II the direct continuation of the layer I, the layer III the direct continuation of the layer II, etc.

Fig. 2.—Inside structure of multilayer coil.

Fig. 3.—Diagram showing position of layers in multilayer coil.



Let now, more generally, ABCD (see fig. 3) be the cross section of the coil. Let the horizontal lines such as $E_1 E_2$ indicate the position of the layers. Let (1) and (2) be the terminals of the coil. Since now

(1) The spacing of the wires in each layer is constant,
(2) The spacing between layers is constant,
(3) The number of turns in each layer and the number of layers are large,
(4) The e.m.f. induced in each turn is the same for all turns,

it is legitimate to conclude that the e.m.f. induced between the terminal (1) and the layer $E_1 E_2$ is proportional to the area

$$(1)\ C E_2 E_1 D\ (1).$$

This fact is true independently of the shape of the contour, ABCD.

In discussing the effective capacity (*loc. cit.*) of a single-layer coil it was only necessary to find a solution of Laplace's equation which became equal to the potential of the coil at the coil and which vanished at infinity. The same is true in the case of multilayer coils.

However, it is not feasible to look for a solution of Laplace's equations in the space between the wires. This solution depends on the total number of wires, on the spacing, insulation, etc. A rigorous solution of the problem offers considerable mathematical difficulties. For this reason a different course is followed in this paper. Instead of studying the small and insignificant variations of potential between the layers, a mean-value treatment of the changes in the field is given. This is, to be sure, approximate. However, if the assumptions (1), (2), (3), (4) are realized, the approximation is justified.

A few words must now be said as to the treatment, by a method of mean values, of the medium in the cross section of the coil.

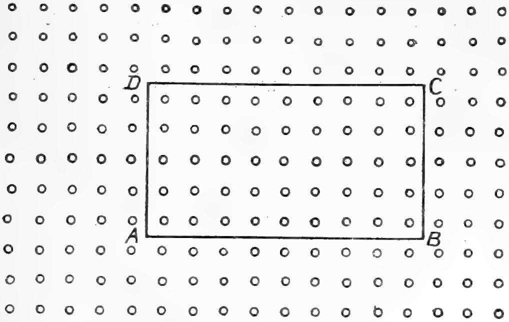
As stated above, the potential of one layer such as $E_1 E_2$ (fig. 3) can be considered as constant. The potential between two consecutive layers does not vary considerably. It is legitimate, therefore, to speak of the average potential at some point in the cross section, meaning thereby the potential of the layer passing through the point or nearest to it. As shown above, this average potential is simply the potential of (1) plus the e.m.f. induced in the area $E_1 E_2 (1)$ (fig. 3), which is proportional to the area $E_1 E_2 (1)$.

From a knowledge of the average potential, the total amount of charge within a given region in the cross section can be obtained by the use of Gauss's Theorem. The same theorem will be used to discuss the charge collecting near the edges of the layers.

Let the rectangle ABCD (fig. 4) be the region in question. Make all the sides lie entirely outside the wires and between the layers as well as the wires of each layer. Now Gauss's theorem will be applied to the volume enclosed by a rectangular prism having unit height and having ABCD for its cross section. The layers of the coil are here taken as parallel to AB. Therefore, by symmetry, there is no flux of the electric intensity across AD and BC. Neither is there any flux across the base—*i. e.*, the rectangle ABCD. Hence the only flux is across the faces whose traces are here shown as AB and CD.

Now the average electric intensity over AB depends on the rate at which the average potential changes in the direction normal to AB in the neighbourhood of AB. If, then, the distance of AB from an arbitrary line parallel

Fig. 4.—Inside structure of multilayer coil.



to AB is y, then the average electric displacement over AB in the direction of y increasing may be written as

$$-\frac{K_e}{4\pi 10^{11}\times 8{\cdot}989}\frac{dV}{dy}\,.\,\overline{AB},$$

where V is the average potential, and K_e is a constant which depends on the relative values of the radius and the distances between two adjacent layers as well as wires in the same layer, and also on the specific inductive capacity of the medium between the wires. (8·989 is the square of 2·9982.) The constant K_e may be called the effective dielectric constant of the composite dielectric formed by the wires and the medium between the wires. In what follows, K_e is set equal to $8{\cdot}989\times 10^{11}\kappa_e$.

Let $$BC = \Delta y.$$

Then the flux out through DC is

$$-\frac{\kappa_e}{4\pi}\left(\frac{dV}{dy}\right)_{y+\Delta y}.\,\overline{AB}.$$

Therefore the flux of the electric displacement out through the surface of the prism is

$$-\frac{\kappa_e\,.\,\overline{AB}}{4\pi}\left[\left(\frac{dV}{dy}\right)_{y+\Delta y}-\left(\frac{dV}{dy}\right)\right]=-\frac{\kappa_e}{4\pi}\frac{d^2V}{dy^2}\,.\,\Delta y\,.\,\overline{AB}$$

if Δy is small. But $\overline{AB}\,.\,\Delta y$ is the volume of the prism.

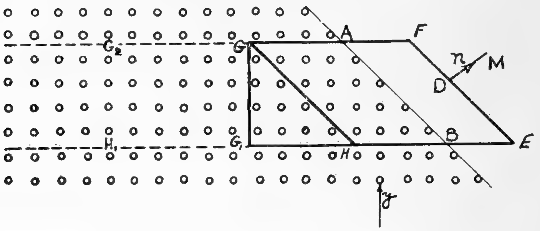
Hence the charge is distributed as if

$$\rho = -\frac{\kappa_e}{4\pi}\frac{d^2V}{dy^2}$$

were its average density.

The above treatment applies to the inside of the coil. The contour of the cross section needs special consideration. Let AB (fig. 5) be a small part of this contour. Draw the parallelogram EFGH with sides EF, GH parallel to AB, and with GF, HE parallel to the layers of the winding. Make GA sufficiently large to obtain a field along GH which is the same as that at similarly situated points G_2, H_1, inside the coil. Make EA sufficiently large to obliterate the irregularities in the field caused by the individual wires. Finally make $\frac{FE}{AG}$ large. Suppose in the space outside the coil a solution of Laplace's equation has been found which at the contour AB becomes equal to the average potential. Then it is clear that at EF this solution gives the actual value of the potential to within the small irregularities which are caused by the individual wires. If V_0 is this potential and K_0 the dielectric constant of the medium outside the cross section of the coil, then letting

Fig. 5.—Structure of multilayer coil near edge.



$$K_0 = 8{\cdot}989 \times 10^{11} \kappa_0,$$

the quantity

$$-\frac{\kappa_0}{4\pi}\frac{\partial V_0}{\partial n}$$

is the component of the electric displacement perpendicular to FE in the direction of DM. The symbol $\frac{\partial}{\partial n}$ denotes here the directional derivative along DM. Hence, if a prism of unit height is built on EFGH as a base,

$$-\frac{\kappa_0}{4\pi}\frac{\partial V_0}{\partial n}\,.\,\overline{FE}$$

is the flux of the electric displacement out through the face of the prism having $\overline{FE}$ for its trace.

Since FG, EH are negligible in comparison with FE, the flux through them may be neglected. It remains to find the flux through GH.

For this purpose, prolong HE and drop a perpendicular to HE from G. Call G_1 the base of this perpendicular. Now Gauss's theorem may be applied to the triangular prism having unit height and GG_1H for base. The point G can always be so chosen as to have the line GG_1 exactly in between the wires of each layer. Then there is no flux across GG_1. Hence the flux out through GH plus the flux out through G_1H is equal to the charge in the volume GG_1H. It must now be remembered that the flux out through GH for the prism GG_1H is the flux into the prism EFGH through the same face. Hence the flux into the prism EFGH is

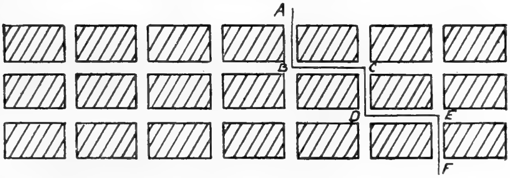
$$-\tfrac{1}{2}\,\overline{G_1H}\,.\,\overline{GH}\,\frac{\kappa_e}{4\pi}\frac{d^2V}{dy^2}-\frac{\kappa_e}{4\pi}\frac{dV}{dy}\,.\,\overline{G_1H}.$$

Hence

$$\sigma=-\frac{\kappa_0}{4\pi}\frac{\partial V_0}{\partial n}+\frac{\kappa_e}{4\pi}\frac{\partial V}{\partial n}.$$

Sometimes an additional consideration is necessary. This happens whenever the line GH of fig. 5 cannot be drawn without cutting the wires. This, for example, would be the case if the wires in each layer were close together, as is seen from fig. 6, where the wires are represented by the small shaded rectangles. However, in this case the zigzag path ABCDE can replace GH so that (2) still holds, where $\overline{G_1H}\frac{d^2V}{dy^2}$ has been left out

Fig. 6.—Possible inside structure of multilayer coil wound with rectangular wires.



because it approaches zero as $\overline{G_1H}$ approaches zero. The expression $\frac{\kappa_e}{4\pi}\frac{G_1H}{AB}\frac{dV}{dy}$ has here been replaced by $\frac{\kappa_e}{4\pi}\frac{\partial V}{\partial n}$ because $\frac{G_1H}{AB} = \cos(G_1HG) = \cos(yn)$. Thus, to summarize, if V is the average potential in the coil, if V_0 is the potential outside which becomes equal to V at the contour of the cross section, then the charges are distributed as if the volume density were

$$\rho = -\frac{\kappa_e}{4\pi}\frac{d^2V}{dy^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the surface density were

$$\sigma = -\frac{\kappa_0}{4\pi}\frac{\partial V_0}{\partial n} + \frac{\kappa_e}{4\pi}\frac{\partial V}{\partial n}, \quad . \quad . \quad . \quad . \quad (2)$$

where

$8{\cdot}989 \times 10^{11}\kappa_0 = K_0 =$ specific inductive capacity of the medium outside the cross section;

$8{\cdot}989 \times 10^{11}\kappa_e = K_e =$ effective specific inductive capacity in the direction *oy* of the medium inside the cross section;

$\frac{\partial}{\partial n}$ is the directional derivative along the outward drawn normal to the contour at the point where σ is taken.

These results will now be used in deriving expressions for the effective capacity of a coil with a circular section, and later will also be applied to coils with square sections.

Coil with Circular Section.

Through the point O (fig. 1) two rectangular axes are now drawn. The axis parallel to the layers is called OX; the axis perpendicular to the layers is called OY. Consider a point P inside the cross section. Its coordinates referred to the axes are (x, y). It was shown that the potential of P exceeds the potential of O by an amount proportional to the area LGMN. This area is

$$\text{LGMN} = a^2\left[\sin^{-1}\frac{y}{a} + \frac{y}{a}\sqrt{1-\frac{y^2}{a^2}}\right].$$

The area of the whole section is

$$\pi a^2.$$

The potential of the upper end of the section is higher than the potential at the lower end by

$$-L\frac{di}{dt},$$

where the current i is reckoned positive when entering the coil through a turn at the lower end of the section and leaving through a turn in the upper. Hence the potential at P exceeds the potential at O by

$$-L\frac{di}{dt}\frac{\sin^{-1}\frac{y}{a}+\frac{y}{a}\sqrt{1-\frac{y^2}{a^2}}}{\pi}.$$

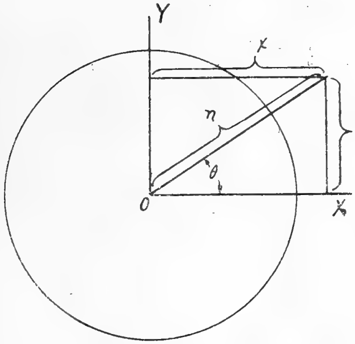


Fig. 7.—Diagram showing co-ordinates used in the case of a coil with circular cross section.

Ungrounded Coil.—Consider the case when the coil is insulated. Then by symmetry the potential at O does not vary. Discarding any constant potential, it is therefore legitimate to state that the potential of O is zero. Therefore the average potential at (x, y) is

$$V=-L\frac{di}{dt}\frac{\sin^{-1}\frac{y}{a}+\frac{y}{a}\sqrt{1-\frac{y^2}{a^2}}}{\pi}. \quad . \quad . \quad . \quad . \quad (3)$$

From this expression ρ can be found by means of equation (1). In order to find σ, V_0 must be found.

In order to find V_0 it is convenient to introduce polar coordinates (r, θ), OX being chosen as the polar axis. The relation of (r, θ) to (x, y) is shown in fig. 7. By virtue of (3), when $r=a$,

$$\left.\begin{aligned} &\mathrm{V}_0=\mathrm{V}=-\frac{\mathrm{L}}{\pi}[\theta+\sin\theta\cos\theta]\frac{di}{dt} \quad \text{if } -\frac{\pi}{2}<\theta<+\frac{\pi}{2} \\ &\text{and} \\ &\mathrm{V}_0=\mathrm{V}=-\frac{\mathrm{L}}{\pi}[\pi-\theta-\sin\theta\cos\theta]\frac{di}{dt} \quad \text{if } \frac{\pi}{2}<\theta<+\frac{3\pi}{2}\,; \end{aligned}\right\} \quad (4)$$

for if $r=a$, then $\mathrm{V}_0=\mathrm{V}$.

Thus V_0 is known over the circumference of a circle. It vanishes at infinity. Therefore, if the value of V_0 over the circumference could be written as a Fourier series in θ, say as

$$(\mathrm{V}_0)_{r=a}=\frac{b_0}{2}+\Sigma\,(b_m\cos m\theta+a_m\sin m\theta), \quad . \quad . \quad (5)$$

then the value at any point (r, θ) $(r>a)$ is

$$\mathrm{V}_0=\frac{b_0}{2}+\Sigma\left(b_m\frac{a^m}{r^m}\cos m\theta+a_m\frac{a^m}{r^m}\sin m\theta\right), \quad . \quad . \quad (6)$$

because this satisfies (1), vanishes at infinity, and satisfies Laplace's equation

$$\frac{\partial^2\mathrm{V}_0}{\partial x^2}+\frac{\partial^2\mathrm{V}_0}{\partial y^2}=0.$$

It remains, therefore, to express the two equations (4) in the form (5).

This is done by defining two functions $f(\theta)$ and $\phi(\theta)$ in the following manner:—

$$f(\theta)=\theta \quad \text{if } -\frac{\pi}{2}<\theta<+\frac{\pi}{2},$$

$$f(\theta)=\pi-\theta \text{ if } \frac{\pi}{2}<\theta<+\frac{3\pi}{2},$$

$f(\theta)$ is periodic of period 2π.

$$\phi(\theta)=\sin\theta\cos\theta \quad \text{if } -\frac{\pi}{2}<\theta<+\frac{\pi}{2},$$

$$\phi(\theta)=-\sin\theta\cos\theta \text{ if } \frac{\pi}{2}<\theta<+\frac{3\pi}{2}$$

$\phi(\theta)$ is periodic of period 2π.

By means of $f(\theta)$ and $\phi(\theta)$, V may be expressed by the formula

$$V = -\frac{L}{\pi}\frac{di}{dt}[f(\theta)+\phi(\theta)].$$

Fig. 8.—Graph of the function $f(\theta)$.

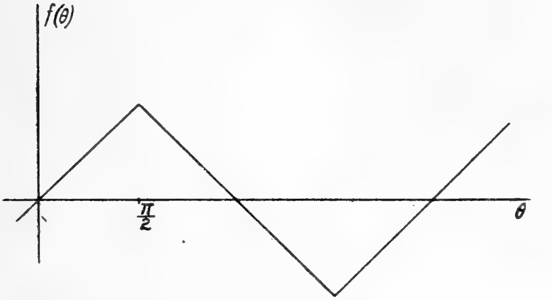
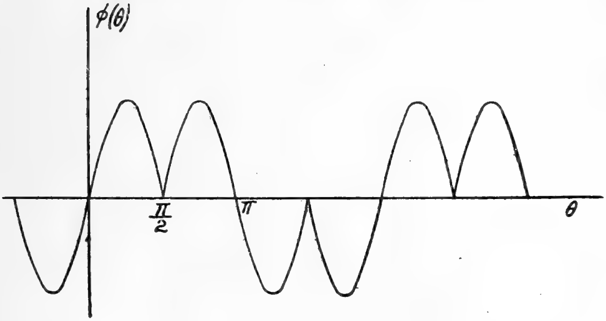


Fig. 8 *a*.—Graph of the function $\phi(\theta)$.



The graphs of $f(\theta)$ and $\phi(\theta)$ are shown in figs. 8 & 8 *a*. Remembering that the series

$$\frac{4}{\pi}(\cos\theta - \tfrac{1}{3}\cos 3\theta + \tfrac{1}{5}\cos 5\theta - \ldots)$$

is 1 from $-\frac{\pi}{2}$ to $+\frac{\pi}{2}$ and -1 from $\frac{\pi}{2}$ to $\frac{3\pi}{2}$ (as may be seen by Fourier's theorem or by expanding $\log\frac{1+x}{1-x}$), it is found at once by integration (which may be shown to be legitimate) that

$$f(\theta) = \frac{4}{\pi}\left(\sin\theta - \frac{1}{3^2}\sin 3\theta + \frac{1}{5^2}\sin 5\theta - \ldots\right)$$

$$= \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-)^n\sin(2n+1)\theta}{(2n+1)^2}. \quad \ldots \ldots \quad (7)$$

Further, $\phi(\theta)$ is an odd function of θ of average value 0. Hence

$$\phi(\theta) = \sum_{m=1}^{\infty} a_m \sin m\theta.$$

Here

$$a_m = \frac{1}{\pi}\int_{-\frac{\pi}{2}}^{\frac{3\pi}{2}} \phi(\theta) \sin m\theta \, d\theta.$$

This gives

$$a_m = (-1)^{\frac{m-3}{2}} \frac{4}{\pi(m^2-4)} \text{ if } m \text{ is odd}$$

and $a_m = 0$ if m is even ($m=2$ included).

Hence

$$\phi(\theta) = \frac{4}{\pi}\sum_{n=0}^{\infty} \frac{(-)^{n-1}\sin(2n+1)\theta}{(2n+1)^2-4}. \quad . \quad (8)$$

Consequently at the boundary (i. e., $r=a$)

$$(V_0)_{r=a} = -\frac{L}{\pi}[f(\theta)+\phi(\theta)]\frac{di}{dt},$$

or by (7) and (8)

$$(V_0)_{r=a} = -\frac{16L}{\pi^2}\frac{di}{dt}\sum_{n=0}^{\infty}\frac{(-)^{n-1}\sin(2n+1)\theta}{(2n+1)^2(2n+3)(2n-1)}.$$

By virtue of (5) and (6)

$$V_0 = -\frac{16L}{\pi^2}\frac{di}{dt}\sum_{n=0}^{\infty}\frac{(-)^{n-1}\left(\frac{a}{r}\right)^{2n+1}\sin(2n+1)\theta}{(2n+1)^2(2n+3)(2n-1)}. \quad . \quad (9)$$

The quantity $\frac{\partial V_0}{\partial n}$ in (2) is now simply $\left(\frac{dV_0}{dr}\right)_{r=a}$. Thus

$$\frac{\partial V_0}{\partial n} = \frac{16L}{\pi^2 a}\frac{di}{dt}\sum_{n=0}^{\infty}\frac{(-)^{n-1}\sin(2n+1)\theta}{(2n+1)(2n+3)(2n-1)}. \quad . \quad (10)$$

This solves the first part of the problem. It now remains to find the quantities $\frac{\partial V}{\partial n}, \frac{d^2V}{dy^2}$.

The first of these is obtained from (3) as

$$\frac{\partial V}{\partial n} = \left(\frac{dV}{dy}\right).\sin\theta = -\frac{2L}{\pi a^2}\frac{di}{dt}.\sqrt{a^2-y^2}\sin\theta, \quad . \quad (11)$$

and similarly

$$\frac{d^2V}{dy^2} = \frac{2L}{\pi a^2}\frac{di}{dt}\frac{y}{\sqrt{a^2-y^2}}. \quad . \quad . \quad . \quad (12)$$

Remembering now that for the point (a, θ)

$$y = a \sin \theta,$$

(11) becomes

$$\frac{\partial V}{\partial n} = \frac{-2L}{\pi a} \frac{di}{dt} \sin \theta \cos \theta. \quad . \quad . \quad . \quad . \qquad (13)$$

Now (1) and (12) yield

$$\rho = -\frac{\kappa_e L}{2\pi^2 a^2} \frac{y}{\sqrt{a^2 - y^2}} \frac{di}{dt}, \quad . \quad . \quad . \quad . \qquad (14)$$

and (2) together with (13) and (10) result in

$$\sigma = -4 \frac{\kappa_0 L}{\pi^3 a} \frac{di}{dt} \sum_{n=0}^{\infty} \frac{(-)^{n-1} \sin (2n+1)\theta}{(2n+1)(2n+3)(2n-1)}$$

$$- \frac{\kappa_e L}{4\pi^2 a} \frac{di}{dt} \sin (2\theta). \quad . \quad . \quad . \quad . \qquad (15)$$

The latter result as well as (13) can be applied only if $-\frac{\pi}{2} < \theta < \frac{\pi}{2}$, because otherwise the radical in (11) must be taken as $-a \cos \theta$. Now the charge in the volume included between y and $y + dy$ is made up of two parts. The first is due to ρ, the second to σ. The part due to ρ is $2l\rho\sqrt{a^2 - y^2}\, dy$, and hence by (14) is

$$-\frac{\kappa_e L}{\pi^2 a^2} l y \frac{di}{dt} dy.$$

The part due to σ is

$$\frac{2l\sigma}{\cos \theta} dy ;$$

and hence by (15)

$$-\left[\frac{8\kappa_0}{\pi^3 a} \sum_{n=0}^{\infty} \frac{(-)^{n-1} \sin (2n+1)\theta}{(2n+1)(2n+3)(2n-1)} + \frac{\kappa_e}{2\pi^2 a} \sin 2\theta\right] lL \frac{di}{dt} \frac{dy}{\cos \theta}.$$

Expressing the result in terms of θ and remembering that $dy = a \cos \theta\, d\theta$, the charge between θ and $\theta + d\theta$ is

$$-\left[\frac{\kappa_e}{\pi^2} \sin 2\theta + \frac{8\kappa_0}{\pi^3} \sum_{n=0}^{\infty} \frac{(-)^{n-1} \sin (2n+1)\theta}{(2n+1)(2n+3)(2n-1)}\right] Ll \frac{di}{dt} d\theta.$$

If this is to be the same as

$$\alpha(\theta) \frac{di}{dt} d\theta,$$

then

$$\frac{\alpha(\theta)}{L} = -\left[\frac{\kappa_e}{\pi^2} \sin 2\theta + \frac{8\kappa_0}{\pi^3} \sum_{n=0}^{\infty} \frac{(-)^{n-1} \sin (2n+1)\theta}{(2n+1)(2n+3)(2n-1)}\right] l. \quad (16)$$

It now remains to find $M(\theta)$. This is obtained from $M(y)$. $M(y)$ itself is given by

$$\frac{M(y)}{L}=\frac{2\sqrt{a^2-y^2}}{\pi a^2}=\frac{2\cos\theta}{\pi a},$$

because the area between y and $y+dy$ is $2\sqrt{a^2-y^2}\,dy$.

Hence

$$\frac{M(\theta)}{L}=\frac{M(y)}{L}\frac{dy}{d\theta}=\frac{2\cos^2\theta}{\pi}. \quad . \quad (17)$$

Therefore

$$C_0=-\int_{\theta=-\frac{\pi}{2}}^{\theta=+\frac{\pi}{2}}\frac{2\cos^2\theta}{\pi}\int_{\theta=-\frac{\pi}{2}}^{\theta}\Bigg[\frac{\kappa_e}{\pi^2}\sin 2\theta + \frac{8\kappa_0}{\pi^3}\sum_{n=0}^{\infty}\frac{(-)^{n-1}\sin(2n+1)\theta}{(2n+1)(2n+3)(2n-1)}\Bigg]l\,d\theta,$$

$$C_0=l\int_{\theta=-\frac{\pi}{2}}^{\theta=+\frac{\pi}{2}}\frac{2}{\pi}\cos^2\theta\Bigg[\frac{\kappa_e}{2\pi^2}(1+\cos 2\theta) + \frac{8\kappa_0}{\pi^3}\sum_{n=0}^{\infty}\frac{(-)^{n-1}\cos(2n+1)\theta}{(2n+1)^2(2n+3)(2n-1)}\Bigg]d\theta,$$

$$C_0=\frac{l}{\pi}\int_{=-\frac{\pi}{2}}^{\theta=+\frac{\pi}{2}}\Bigg[\frac{\kappa_e}{2\pi^2}(1+\cos^2 2\theta+2\cos 2\theta) + \frac{8\kappa_0}{\pi^3}\sum_{n=0}^{\infty}\frac{(-)^{n-1}\{\cos(2n-1)\theta+\cos 2\theta\cos(2n+1)\theta\}}{(2n+1)^2(2n+3)(2n-1)}\Bigg]d\theta$$

$$=\frac{l}{\pi}\Bigg[\frac{3\kappa_e}{4\pi}+\frac{8\kappa_0}{\pi^3}\sum_{n=0}^{\infty}\frac{2}{(2n+1)^2(2n+3)(2n-1)}\Bigg(-\frac{1}{2n+1}+\frac{1}{2(2n+3)}+\frac{1}{2(2n-1)}\Bigg)\Bigg]$$

$$=\frac{l}{\pi}\Bigg[\frac{3\kappa_e}{4\pi}+\frac{64\kappa_0}{\pi^3}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^3(2n+3)^2(2n-1)^2}\text{ farads.}$$

The series $\sum_{n=0}^{\infty}\frac{1}{(2n+1)^3(2n+3)^2(2n-1)^2}$ is very rapidly convergent. The calculation of a few terms gives for its value

$$0{\cdot}1126.$$

Hence

$$C_0 = 0{\cdot}07599\,\kappa_e l+0{\cdot}07398\,\kappa_0 l, \quad . \quad . \quad (18)$$

or in terms of K_e, K_0

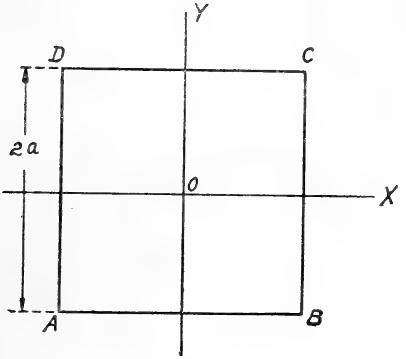
$$C_0 = 10^{-12}[0{\cdot}08453\,K_e+0{\cdot}08230\,K_0]l \text{ farads}$$

$$= (0{\cdot}08453\,K_e+0{\cdot}08230\,K_0)l \text{ micromicrofarads.} \quad (18')$$

Coil with a Square Section.

The coil with a square section can also be studied by the same method. The side of the square is denoted by $2a$. The origin of co-ordinates is placed at the centre of the square. The layers are supposed to be arranged parallel to one of the sides. One of the coordinate axes is drawn parallel to that side and the other perpendicular to it. The first is called OX and the second OY. (See fig. 9.)

Fig. 9.—Diagram of coil with square cross section.



In this case, if the coil is ungrounded, V at O is zero. Hence V at (x, y) is

$$\mathrm{V}=-\frac{y\,.\,2a}{4a^2}\mathrm{L}\frac{di}{dt}=-\frac{y}{2a}\mathrm{L}\frac{di}{dt}, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

because the e.m.f. induced between two layers is proportional to the area of the cross-section subtended by the layers, since the diameter of the coil was assumed to be large in comparison with the dimensions of its cross-section.

It is clear that $\frac{d^2\mathrm{V}}{dy^2}=0$. Therefore $\rho=0$. It remains to compute σ. It is seen from (2) that σ is made up of two parts. The first of these contains κ_0 as a factor, and the second similarly involves κ_e. It is clear that at BC and AD (fig. 9) $\frac{\partial \mathrm{V}}{\partial n}=0$. Hence [see equations (1), (2)] the only contributions to the term involving κ_e are given by AB and CD, *i.e.* by the end layers of the coil. At CD, $\frac{\partial \mathrm{V}}{\partial n}=\frac{d\mathrm{V}}{dy}$ and at AB, $\frac{\partial V}{\partial n}=-\frac{dV}{dy}$. Hence at CD the part of σ involving κ_e is

$$-\frac{\kappa_e}{2a}\frac{L}{4\pi}\frac{di}{dt},$$

and at AB this part of σ is

$$+\frac{\kappa_e}{2a}\frac{L}{4\pi}\frac{di}{dt}.$$

But the potential of DC exceeds the potential of AB by

$$-L\frac{di}{dt}.$$

Therefore the effect of this part of σ is precisely the same as would be caused by a condenser of capacity

$$\frac{\kappa_e l}{4\pi}.$$

This part of the effective capacity can be interpreted as the capacity between two conducting sheets separated by a medium of specific inductive capacity K_e at a distance $2a$, the area of each sheet being $2al$. The contribution of the above quantity to C_0 will be called

$$C_0'=\frac{\kappa_e l}{4\pi}=0\cdot0796\,\kappa_e l. \quad . \quad . \quad . \quad . \quad (20)$$

Now V_0 must be found. For this purpose it is necessary to solve the potential problem in two dimensions for the case of a square. This can be done by means of elliptic functions in various ways. The one given here is convenient on account of the fact that rapidly converging series are obtained for the results. Also it can be understood without any knowledge of elliptic functions.

Let $$z=x+jy \quad (j=\sqrt{-1}),$$

and consider the transformation defined by the differential equation

$$\frac{dz}{d\tau}=A\epsilon^{j\frac{\pi}{4}}(1-\tau^{-4})^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad (21)$$

where A is a constant and ϵ is the natural base. It will be shown presently that this transformation has the property of transforming the unit circle in the τ plane into a square in the z plane. Also it transforms the region outside the unit circle into the region outside the square.

Before proving the above-mentioned properties, a few words must be said as to the meaning of the square root in (21), because the square root is a two-valued function, and confusion will be caused unless it is known definitely what branch of the function is used. In the following, the only case of interest is that of

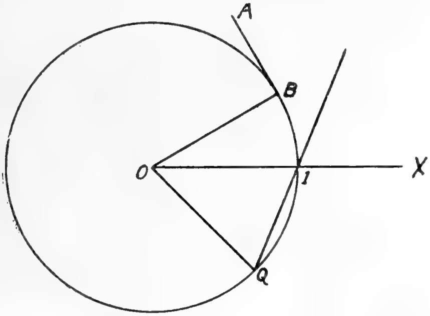
$$|\tau| > 1.$$

This excludes the possibility of negative values of the real part of

$$1-\tau^{-4}.$$

The square root will then be chosen so as to have its real part always positive or zero. This involves a cut along the negative of the axis of reals in the plane of $1-\tau^{-4}$. Since, however, the real part of $1-\tau^{-4}$ is never negative, no discontinuity in $(1-\tau^{-4})^{\frac{1}{2}}$ is introduced by the cut.

Fig. 10.—Illustration of proof of conformal transformation of the outside of a square.



Consider now the value of $\frac{dz}{d\tau}$ given by (21) in the case of τ moving on the unit circle (see fig. 10) in the counter-clockwise direction starting at the point (1). At 1, $\frac{dz}{d\tau}=0$, which shows that 1 is a branch of the transformation (21). The velocity of motion of z is therefore zero as τ approaches 1 with a constant velocity. But if τ is slightly different from 1 and lies on the unit circle, say if τ occupies the position B (fig. 10), then the point τ^{-4} has the position Q on the same circle such that $4\angle \mathrm{B}01=\angle 10\mathrm{Q}$.

The stroke Q1 represents then in magnitude and direction the quantity $1-\tau^{-4}$. Now the angle which this stroke makes with the positive direction of the axis of x is readily shown to be

$$\frac{\pi}{2}-2\angle \mathrm{B}01.$$

Hence the argument of $(1-\tau^{-4})^{\frac{1}{2}}$ is $\frac{\pi}{2}-\angle \mathrm{B}\,01$ as long as this quantity is less than π and greater than $-\pi$ (by the definition of the meaning of the square root). Now draw BA tangent to the unit circle at B. The argument of the stroke BA is

$$\frac{\pi}{2}+\angle \mathrm{B}\,01.$$

But this is the argument of $d\tau$ in (21). Therefore, by (21), the argument of dz is

$$\frac{\pi}{2}+\angle \mathrm{B}\,01+\frac{\pi}{4}-\angle \mathrm{B}\,01+\frac{\pi}{4}=\pi.$$

This means that as B moves on the unit circle, z moves in a straight line parallel to the axis of reals and in the negative direction.

Such is the case as long as the argument of $(1-\tau^{-4})^{\frac{1}{2}}$ is $\frac{\pi}{4}-\angle \mathrm{B}01$. Consider now the behaviour of arg. $(1-\tau^{-4})$. As B moves from 1 to $\sqrt{j}$, Q moves from 1 to -1 so that arg. $(1-\tau^{-4})$ varies from $\frac{\pi}{2}$ to 0. Further, as B moves from $\sqrt{j}$ to j, Q follows the upper part of the unit circle and arg. $(1-\tau^{-4})$ varies from 0 to $-\frac{\pi}{2}$. Within this region arg. $(1-\tau^{-4})$ is $\frac{\pi}{2}-2\angle \mathrm{B}01$ and, therefore, arg. $(1-\tau^{-4})^{\frac{1}{2}}$ is $\frac{\pi}{4}-\angle \mathrm{B}01$.

But as soon as τ crosses j, the principal value of the arg. $(1-\tau^{-4})$ must again be taken as $\frac{\pi}{2}$, for otherwise the real part of the square root will be negative. Hence, from j on, arg. $(1-\tau^{-4})^{\frac{1}{2}}$ must be taken as

$$\frac{\pi}{4}-\left(\angle \mathrm{B}\,01-\frac{\pi}{2}\right).$$

As before, arg. $d\tau$ is

$$\frac{\pi}{2}+\angle \mathrm{B}\,01,$$

and, therefore, by (21)

$$\text{arg. } dz=\frac{\pi}{2}+\angle \mathrm{B}\,01+\frac{\pi}{4}-\left(\angle \mathrm{B}\,01-\frac{\pi}{2}\right)+\frac{\pi}{4}=\frac{3\pi}{2}.$$

Thus as τ moves from j to -1, z moves in a straight line parallel to the axis of pure imaginaries and in the negative sense.

Similarly it may be shown that as τ moves from -1 to $-j$, z moves in a straight line parallel to the axis of reals and in the positive sense. Finally, as τ moves from $-j$ to $+1$, z moves in a straight line parallel to the axis of pure imaginaries in the positive sense.

It will now be shown that as τ returns to the value 1, z returns to its original value. In fact by (21), if

$$\tau' = \epsilon^{j\frac{\pi}{4}}\tau,$$

$$\left|\frac{dz}{d\tau'}\right| = \left|\frac{dz}{d\tau}\right|.$$

Therefore, the length of the straight line corresponding to the values of τ between 1 and j is the same as that of the straight line corresponding to the values of τ between j and -1. Similarly the remaining two straight lines are equal to the ones mentioned above. Thus the figure is a convex rectangle with all sides equal, and hence is closed and is a square.

From the finiteness and continuity of the functions on the right-hand side of (21), it follows that $\frac{dz}{d\tau}$ is finite, single-valued and continuous for $\tau>1$. Also if $|\tau|$ is large, $\frac{dz}{d\tau}$ approaches $\epsilon^{\frac{\pi}{4}}$. Therefore, changes in τ call for equal (in absolute value) changes in z. Hence parts of the τ plane lying at an infinite distance from the origin correspond to parts of the z plane also lying at an infinite distance from the origin.

If $|\tau|>1$, the right-hand side of (21) may be expanded by the binomial theorem, viz.,

$$\frac{dz}{d\tau} = \mathrm{A}\epsilon^{j\frac{\pi}{4}}\left[1-\sum_{s=1}^{\infty} p_s\tau^{-4s}\right],$$

$$\text{where} \quad p_s = \left|\frac{1.3.5\ldots(2s-3)}{2.4.6\ldots 2s}\right|. \quad . \quad (22)$$

Hence by integration a particular solution for z is

$$z = \mathrm{A}\epsilon^{j\frac{\pi}{4}}\left[\tau+\sum_{s=1}^{\infty} p_s\frac{\tau^{-(4s-1)}}{4s-1}\right]. \quad . \quad . \quad . \quad (23)$$

This particular solution for z makes the centre of the square coincident with the origin. Other solutions may be obtained by adding a constant to the above.

In the applications to the coil, it is desirable to transform τ in such a way as to make the real part of the new variable $(w=u+jv)$ have a constant value at the surface of the square. This is accomplished by writing

$$\tau = \epsilon^{u+jv}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

so that (23) becomes

$$z = \mathrm{A}\epsilon^{j\frac{\pi}{4}}\left[\epsilon^{u+jv} + \sum_{s=1}^{\infty} p_s \frac{\epsilon^{-(4s-1)(u+jv)}}{4s-1}\right]. \quad . \quad . \quad (25)$$

If $u=0$, $|\tau|=1$ in virtue of (24) and, therefore, z is on the unit circle. Thus (u, v) will now be curvilinear co-ordinates in the plane (x, y). Only positive values of u are considered because only positive values of $|\tau|-1$ are required. A curve corresponding to $u=$constant is a closed curve. If $u=0$, this curve is the square. If $u=\infty$, $\tau=\infty$ and therefore, as was previously shown, the infinitely distant part of the z plane is attained. Further, there is no difficulty in showing from (25) that larger values of u correspond to curves enclosing those corresponding to smaller values of u. If u is large, (25) becomes $z=\mathrm{A}\epsilon^{u+j(v+\frac{\pi}{4})}$ and for varying v represents a circle with a radius $\mathrm{A}\epsilon^{u}$. The value $v=0$ corresponds to a point subtending at the origin an angle $\frac{\pi}{4}$ with the axis of reals. Similarly on the square $u=0$, $v=0$ gives a point subtending an angle $\frac{\pi}{4}$ with the axis of reals at the origin, and the points $v=\frac{\pi}{2}, \pi, \frac{3\pi}{2}$ are as indicated in fig. 11.

The value of A in terms of a is clearly

$$\mathrm{A} = \frac{a\sqrt{2}}{1+\sum_{s=1}^{\infty}\frac{p_s}{4s-1}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

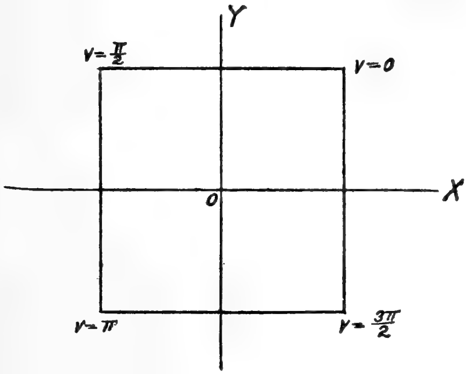
since for $v=0$, $z=1+j$;

and other expressions may also be given.

In the plane of z, the real part of any monogenic function of $u+jv$ is a solution of Laplace's equation

$$\frac{\partial^2 V}{\partial x^2}+\frac{\partial^2 V}{\partial y^2} = 0.$$

Fig. 11.—Distribution of the parameter v on the square.



In the case considered, V must vanish at infinity and must be $-\frac{L}{2}\frac{y}{a}\frac{di}{dt}$ at the surface of the coil, *i. e.* at $u=0$. But by (25), at $u=0$

$$y = A\left[\sin\left(v+\frac{\pi}{4}\right)-\sum_{s=0}^{\infty} p_s \frac{\sin\left[(4s-1)v-\frac{\pi}{4}\right]}{4s-1}\right]. \qquad (26\,a)$$

It is clear then that

$$V=-\frac{AL}{2a}\left(\frac{di}{dt}\right)\left[\epsilon^{-u}\sin\left(v+\frac{\pi}{4}\right)\right.$$

$$\left.-\sum_{s=1}^{\infty} p_s\epsilon^{-(4s-1)u}\frac{\sin\left\{(4s-1)v-\frac{\pi}{4}\right\}}{4s-1}\right]. \qquad (27)$$

is the solution required because it degenerates into $-\frac{L}{2}\frac{y}{a}\frac{di}{dt}$ for $u=0$ in virtue of (26), because it vanishes at infinity, and because it may be shown to be the real part of

$$-j\frac{\mathrm{AL}}{2a}\frac{di}{dt}\left[\epsilon^{-\left(u+jv+j\frac{\pi}{4}\right)}-\sum_{s=1}^{\infty}p_s\frac{\epsilon^{-(4s-1)(u+jv)+j\frac{\pi}{4}}}{4s-1}\right].$$

At any point on the square the charge density due to V_0 is

$$\sigma=-\frac{\kappa_0}{4\pi}\frac{\partial \mathrm{V}}{\partial n}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (28)$$

where as before κ_0 is $\frac{\mathrm{K}_0}{8{\cdot}989\times 10^{11}}$, K_0 being the dielectric constant of the medium outside the square and $\frac{\partial}{\partial n}$ being the directional derivative along the normal drawn outward at the surface of the square. Since that surface has the equation $u=0$,

$$\sigma=-\frac{\kappa_0}{4\pi}\frac{\partial \mathrm{V}}{\partial u}\left|\frac{dw}{dz}\right|.$$

Let as usual l denote the perimeter of one turn and ds an element of length along the perimeter of the square reckoned positive when in the direction of v increasing. The amount of charge in the element ds is

$$-\frac{\kappa_0}{4\pi}l\frac{\partial \mathrm{V}}{\partial u}\left|\frac{dw}{dz}\right|ds.$$

If now dv should stand for the change in v corresponding to ds, $\frac{ds}{dv}=\left|\frac{dz}{dw}\right|$ because the transformation used is conformal. Hence the amount of charge between v and $v+dv$ is

$$\mathrm{Q}(v)\,dv=-\frac{\kappa_0 l}{4\pi}\left(\frac{\partial \mathrm{V}}{\partial u}\right)_{u=0}dv.$$

Hence, since the function $\alpha(v)$ is $\frac{\mathrm{Q}(v)}{\frac{di}{dt}}$, then by (27)

$$\alpha(v)=-\frac{\kappa_0 l\mathrm{LA}}{8\pi a}\left[\sin\left(v+\frac{\pi}{4}\right)-\sum_{s=1}^{\infty}p_s\sin\left\{(4s-1)v-\frac{\pi}{4}\right\}\right]. \quad . \quad . \quad . \qquad (29)$$

It is now also necessary to find $\mathrm{M}(v)$. This is found from $M(y)$, which is readily seen to be

$$M(y) = \frac{L}{2a},$$

because the e.m.f. induced between two layers is proportional to the area enclosed by the layers, so that remembering (26 *a*)

$$M(v) = M(y)\frac{dy}{dv} = \frac{LA}{2a}\left[\cos\left(v+\frac{\pi}{4}\right)\right.$$

$$\left. - \sum_{s=1}^{\infty} p_s \cos\left\{(4s-1)v-\frac{\pi}{4}\right\}\right]. \quad . \quad (30)$$

Care must now be exercised to differentiate between the four sides of the square. In formula (30) it was assumed that each layer of the coil is considered once. For this reason the expression $\alpha(v)$ given in (29) must be modified because $\alpha(v)$ refers separately to all values of v, and, therefore, does not combine the charges on the side for which $\frac{3\pi}{2} < v < 0$ with the equal and similarly situated charges on the side for which $\frac{\pi}{2} < v < \pi$. Thus it is necessary to double $\alpha(v)$ as given by (29), and to discuss only the range of values of v between $+\frac{3\pi}{2}$ and $+2\pi$. In addition, of course, the charges on the face (see fig. 11) $\left(v=0,\ v=\frac{\pi}{2}\right)$ as well as those on $\left(v=\pi,\ v=\frac{3\pi}{2}\right)$ must be computed. These charges are collected on the outside layer, and have simply the effect of a capacity across the whole coil. Thus the effect of the charges on the surface divides itself into two. The first of these is that of the charges on the faces $y=\pm a$. The second is that on the faces $x=\pm a$. The contribution of the first to C_0 is denoted by C_0'' and that of the second by C_0'''. The computation of C_0''' will be effected first, and then C_0'' will also be obtained.

For C_0''' the formula

$$C_0''' = \int_{v=\frac{3\pi}{2}}^{2\pi} \frac{M(v)}{L} \left\{\int_{v=\frac{3\pi}{2}}^{v} \frac{\bar{\sigma}(v)}{L}\, dv\right\} dv$$

holds, where, as has been shown in the preceding paragraph,

$M(v)$ has the value given in (30) and $\bar{\alpha}(v)$ has double the value of $\alpha(v)$ given in (29), *i. e.*, $\bar{\alpha}(v)=2\alpha(v)$.

$$\begin{aligned} C_0''' = -\frac{\kappa_0 l A^2}{8\pi a^2}\int_{v=\frac{3\pi}{2}}^{2\pi} \Bigg\{ & \cos\left(v+\frac{\pi}{4}\right) \\ & -\sum_{s=1}^{\infty} p_s \cos\left[(4s-1)v-\frac{\pi}{4}\right]\Bigg\}\Bigg\{\int_{v=\frac{3\pi}{2}}^{v}\Bigg[\sin\left(v+\frac{\pi}{4}\right) \\ & -\sum_{s=1}^{\infty} p_s \sin\left\{(4s-1)v-\frac{\pi}{4}\right\}\Bigg]dv\Bigg\}, \end{aligned}$$

$$\begin{aligned} C_0''' = +\frac{\kappa_0 l A^2}{8\pi a^2}\int_{v=\frac{3\pi}{2}}^{2\pi} \Bigg[& \cos\left(v+\frac{\pi}{4}\right) \\ & -\sum_{s=1}^{\infty} p_s \cos\left\{(4s-1)v-\frac{\pi}{4}\right\}\Bigg]\Bigg[\cos\left(v+\frac{\pi}{4}\right)-\frac{1}{\sqrt{2}} \\ & -\sum_{s=1}^{\infty}\frac{\cos\left[(4s-1)v-\frac{\pi}{4}\right]-\frac{1}{\sqrt{2}}}{4s-1}\Bigg]\,dv, \end{aligned}$$

$$\begin{aligned} C_0''' = \frac{\kappa_0 l A^2}{8\pi a^2}\int_{v=\frac{3\pi}{2}}^{2\pi} \Bigg\{ & \cos^2\left(v+\frac{\pi}{4}\right)-\frac{1}{\sqrt{2}}\cos\left(v+\frac{\pi}{4}\right) \\ & -\sum_{s=1}^{\infty} p_s\Bigg[\cos\left\{(4s-1)v-\frac{\pi}{4}\right\}\cos\left(v+\frac{\pi}{4}\right) \\ & \qquad -\frac{1}{\sqrt{2}}\cos\left\{(4s-1)v-\frac{\pi}{4}\right\}\Bigg] \\ & -\sum_{s=1}^{\infty} p_s\frac{\cos\left(v+\frac{\pi}{4}\right)\cos\left\{(4s-1)v-\frac{\pi}{4}\right\}-\frac{1}{\sqrt{2}}\cos\left(v+\frac{\pi}{4}\right)}{4s-1} \\ & \qquad -\frac{1}{\sqrt{2}}\cos\left\{(4s_1-1)v-\frac{\pi}{4}\right\} \\ & +\sum_{s_1,\,s_2=1,\,2,\,3}^{\infty}{}' p_{s_1}p_{s_2}\frac{\cos\left\{(4s_1-1)v-\frac{\pi}{4}\right\}\cos\left\{(4s_2-1)v-\frac{\pi}{4}\right\}\wedge}{4s_2-1} \\ & +\sum_{s=1}^{\infty} p_s^2\frac{\cos^2\left\{(4s-1)v-\frac{\pi}{4}\right\}-\frac{1}{\sqrt{2}}\cos\left\{(4s-1)v-\frac{\pi}{4}\right\}}{4s-1}\Bigg\}\,dv, \end{aligned}$$

where $\sum\limits_{s_1, s_2=1,2,3}^{\infty}{}'$ is extended over all values of s_1, s_2 with the exception of the case when $s_1=s_2$. The integrals in this expression are all of either of the types:

$$\int_{\frac{3\pi}{2}}^{\frac{\pi}{2}} \cos\left(v+\frac{\pi}{4}\right)dv, \qquad \int_{\frac{3\pi}{2}}^{2\pi} \cos\left\{(4s-1)v-\frac{\pi}{4}\right\}dv,$$

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos^2\left(v+\frac{\pi}{4}\right)dv, \qquad \int_{\frac{3\pi}{2}}^{2\pi} \cos^2\left\{(4s-1)v-\frac{\pi}{4}\right\}dv,$$

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos\left(v+\frac{\pi}{4}\right)\cos\left\{(4s-1)v-\frac{\pi}{4}\right\}dv,$$

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos\left\{(4s_1-1)v-\frac{\pi}{4}\right\}\cos\left\{(4s_2-1)v-\frac{\pi}{4}\right\}dv.$$

For these, direct integration gives

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos\left(v+\frac{\pi}{4}\right)dv = \sqrt{2},$$

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos\left\{(4s-1)v-\frac{\pi}{4}\right\}dv = -\frac{\sqrt{2}}{4s-1},$$

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos^2\left(v+\frac{\pi}{4}\right)dv = \frac{\pi}{4}+\frac{1}{2},$$

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos^2\left\{(4s-1)v-\frac{\pi}{4}\right\}dv = \frac{\pi}{4}-\frac{1}{8s-2},$$

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos\left(v+\frac{\pi}{4}\right)\cos\left\{(4s-1)v-\frac{\pi}{4}\right\}dv = -\frac{1}{4s-2},$$

$$\int_{\frac{3\pi}{2}}^{2\pi} \cos\left\{(4s_1-1)v-\frac{\pi}{4}\right\}\cos\left\{(4s_2-1)v-\frac{\pi}{4}\right\}dv$$

$$= -\frac{1}{4s_1+4s_2-2}.$$

Substituting these values into the value of C_0''' just found,

$$C_0''' = \frac{\kappa_0 l A^2}{8\pi a^2}\left[-\frac{1}{2} + \sum_s \frac{4s p_s}{(4s-1)(4s-2)} + \frac{\pi}{4}\left(1 + \sum_s \frac{p_s^2}{4s-1}\right.\right.$$

$$\left.\left. + \sum_{s_1, s_2} \frac{p_{s_1} p_{s_2}}{(4s_1-1)(4s_1+4s_2-2)}\right)\right], \quad \ldots \quad (31)$$

where now the result is expressed without making use of the notation Σ' but using throughout the ordinary Σ.

Now C_0'' must be calculated by finding the charge on the side of the square given by values of v included between 0 and $\frac{\pi}{2}$. If this charge is Q,

$$C_0'' = -\frac{Q}{L\left(\frac{di}{dt}\right)}, \quad \ldots\ldots \quad (32)$$

because $-L\left(\frac{di}{dt}\right)$ is the excess of the potential of that plate over the potential of the opposite plate.

In virtue of (29), the charge between v and $v+dv$ is

$$\frac{di}{dt}\alpha(v)\,dv = -\frac{\kappa_0 l L A}{8\pi a}\left(\frac{di}{dt}\right)\left[\sin\left(v+\frac{\pi}{4}\right)\right.$$

$$\left. - \sum_{s=1}^{\infty} p_s \sin\left\{(4s-1)v - \frac{\pi}{4}\right\}\right],$$

so that the total charge on the face considered is

$$-\frac{\kappa_0 l L A}{8\pi a}\frac{di}{dt}\int_0^{\frac{\pi}{2}}\left[\sin\left(v+\frac{\pi}{4}\right) - \sum_{s=1}^{\infty} p_s \sin\left\{(4s-1)v - \frac{\pi}{4}\right\}dv,\right.$$

and therefore by (32)

$$C_0'' = \frac{\kappa_0 l A}{8\pi a}\int_0^{\frac{\pi}{2}}\left[\sin\left(v+\frac{\pi}{4}\right) - \sum_{s=1}^{\infty} p_s \sin\left\{(4s-1)v - \frac{\pi}{4}\right\}\right]dv, \quad \ldots \quad (33)$$

or performing the integrations

$$C_0'' = \frac{\kappa_0 l A\sqrt{2}}{8\pi a}\left[1 - \sum_{s=1}^{\infty} \frac{p_s}{4s-1}\right]. \quad \ldots \quad (34)$$

Substituting (26) into (31) and (34),

$$C_0{}' = \frac{\kappa_0 l}{4\pi} \frac{1 - \sum\limits_{s=1}^{\infty} \dfrac{p_s}{4s-1}}{1 + \sum\limits_{s=1}^{\infty} \dfrac{p_s}{4s-1}}. \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Thus formulæ (20), (31), (35) give $C_0{}'$, $C_0{}''$, $C_0{}'''$. Hence C_0 is obtained as

$$C_0 = C_0{}' + C_0{}'' + C_0{}'''.$$

The expression for $C_0{}'$ is in a form suitable for numerical computation. It remains to transform (31) and (35) into more convenient expressions.

This may be done by formula (26), which gives

$$1 + \sum_{s=1}^{\infty} \frac{p_s}{4s-1} = \frac{a\sqrt{2}}{A}. \quad . \quad . \quad . \quad . \quad . \quad (36)$$

An expression for $\frac{a}{A}$ may now also be obtained in a different form by making $v = -\frac{\pi}{4}$ in (25). This gives for x, which is equal to a for the above value of v,

$$A\left[1 + \sum_s \frac{(-)^s p_s}{4s-1}\right];$$

so that

$$\frac{a}{A} = 1 + \sum_s \frac{(-)^s p_s}{4s-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

In this series the terms are alternately positive and negative, so that the error committed is always less in absolute value than the last term left out. Thus, taking the first six terms of the series (37), the error committed is less than 0·001. A calculation gives

$$\frac{a}{A} = 0{\cdot}847. \quad . \quad . \quad . \quad . \quad . \quad . \quad (37\,a)$$

The value of $\frac{a}{A}$ thus being known, the double series

$$\Sigma \frac{p_{s_1} p_{s_2}}{(4s_1 - 1)(4s_1 + 4s_2 - 2)}$$

which occurs in (31) will be expressed in terms of $\Sigma \frac{p_s}{4s-1}$.

and hence by means of (36) through $\frac{a}{\mathrm{A}}$. The transformation is effected by means of the identity

$$\sum_{s_1 s_2} \frac{p_{s_1} p_{s_2}}{(4s_1-1)(4s_1+4s_2-2)}$$
$$= \sum \frac{p_{s_1} p_{s_2}}{4s_2-1} \left(-\frac{1}{4s_1+4s_2-2} + \frac{1}{4s_1-1}\right),$$

which gives

$$\sum_{s_1 s_2} \frac{p_{s_1} p_{s_2}}{(4s_1-1)(4s_1+4s_2-2)} = \tfrac{1}{2} \sum \frac{p_{s_1} p_{s_2}}{(4s_1-1)(4s_2-1)}$$
$$= \tfrac{1}{2} \left(\sum_{s=1}^{\infty} \frac{p_s}{4s-1} \right)^2,$$

or substituting (36),

$$\sum_{s_1 s_2} \frac{p_{s_1} p_{s_2}}{(4s_1-1)(4s_1+4s_2-2)} = \tfrac{1}{2} \left(\frac{a\sqrt{2}}{\mathrm{A}} - 1 \right)^2.$$

Similarly in (35) the substitution of (36) gives

$$\mathrm{C}_l'' = \frac{\kappa_0 l}{4\pi} \left(\frac{\mathrm{A}}{a} \sqrt{2} - 1 \right) = 0{\cdot}0532\, \kappa_0 l. \quad . \quad . \quad . \quad (38)$$

Further, the summation $\sum_{1}^{\infty} \frac{4s\, p_s}{(4s-1)(4s-2)}$ occurring in (31) is equal to

$$\sum_{1}^{\infty} \frac{p_s}{4s-1} + 2 \sum_{1}^{\infty} \frac{p_s}{(4s-1)(4s-2)},$$

or, using (36),

$$\sum_{1}^{\infty} \frac{4s\, p_s}{(4s-1)(4s-2)} = \frac{a\sqrt{2}}{\mathrm{A}} - 1 + 2 \sum_{1}^{\infty} \frac{p_s}{(4s-1)(4s-2)}.$$

A calculation of the last series shows it to be 0·0871. This value together with (37 *a*) gives

$$\sum_{1}^{\infty} \frac{4s\, p_s}{(4s-1)(4s-2)} = 0{\cdot}3719. \quad . \quad . \quad . \quad (39)$$

Finally the quantity $\frac{\pi}{4}\left(1 + \sum_{1}^{\infty} \frac{p_s^2}{4s-1}\right)$ in (31) must be calculated. The series in parentheses is rapidly convergent, and a calculation gives for it 1·086, so that

$$\frac{\pi}{4}\left(1 + \sum_{1}^{\infty} \frac{p^2}{4s-1}\right) = 0{\cdot}853. \quad . \quad . \quad . \quad (40)$$

Substituting (40), (39), (37), (37 *a*) into (31),

$$C_0''' = \frac{\kappa_0 l}{8\pi(0{\cdot}847)^2}\left[-\tfrac{1}{2}+0{\cdot}371+0{\cdot}853+\tfrac{1}{2}(0{\cdot}198)^2\right]$$
$$= 0{\cdot}0412\kappa_0 l. \quad . \quad (41)$$

Now substituting (38), (41), (20) into

$$C_0 = C_0' + C_0'' + C_0''',$$

it follows that

$$C_0 = 0{\cdot}0796\,\kappa_e l + 0{\cdot}0944\,\kappa_0 l,$$

$$C_0 = 10^{-12}[0{\cdot}886\,K_e l + 0{\cdot}1050\,K_0 l] \text{ farads}$$

$$= [0{\cdot}0886\,K_e l + 0{\cdot}1050\,K_0 l] \text{ micromicrofarads.} \quad (42)$$

Both (18′) and (42) involve the constant K_e. As stated previously, a theoretical derivation of K_e is, in general, difficult. However, an experimental investigation is possible. For this purpose, it is only necessary to introduce a slab of the complex medium between two plates of a condenser and measure the increase in capacity caused thereby, treating the slab as if it were a homogeneous dielectric. Of course, care must be taken to have the layers of the complex medium parallel to the condenser plates. One must also remember that the mean value treatment can be applied only in the case of coils having a large number of turns per layer.

In some special cases the value of K_e may be obtained without difficulty. Such is the case, for example, of a winding such as shown in fig. 6, when adjacent turns almost touch. In such a case the effective dielectric constant K_e is $\frac{h}{h'}K$, where K is the dielectric constant of the medium between turns and where h is the distance between homologous points of two layers, while h' is the shortest distance between two layers. This principle may be extended also to the case of wires of circular cross section if the distance between layers is large and the winding of each layer is close, provided each layer is replaced by an equivalent layer of uniform thickness, this thickness being made equal to the average double ordinate of the circle.

A few words must be said as to the meaning of l in (18′) and (42). Strictly speaking, the derivation given applies only to the case when the perimeter of one turn is the same as that of any other. However, the considerations as to the distribution of charge will apply approximately even if the turns are not of equal perimeter. In this case l becomes indefinite. If the cross section is symmetrical about a line through its centroid parallel to the axis, l may be taken simply as the perimeter of the turn through the centroid because the mean between the perimeters of two turns symmetrically situated as to the centroid is that value of l, and because the charge density on these turns is the same.

Summary.

A method of calculating the effective capacity of multilayer coils has been given. It has been shown that the average density of volume and surface charge may be obtained in terms of a constant K^e which depends on the spacing between the turns of the coil and the insulation used. This constant is analogous to the dielectric constant of a homogeneous medium.

The method has been applied to the case of a coil having a circular section, and also to the case of a coil with a square section.

The results are:

$$C_0 = (0{\cdot}08453\,K_e + 0{\cdot}08230\,K_0)l \text{ micromicrofarads}$$

for the case of a coil with circular section

and

$$C_0 = (0{\cdot}0886\,K_e + 0{\cdot}1050\,K_0)l \text{ micromicrofarads}$$

for the case of a coil with square section.

Here K_0 is the dielectric constant of the medium outside the coil, K_e is the effective dielectric constant of the medium inside the coil, l is the perimeter of a single turn passing the centre of the cross section. In both cases, the diameter of the coil is taken to be large in comparison with the maximum dimension of the cross section, the winding is assumed to be close, the number of turns large, and the coil itself is taken to be insulated from all objects except the tuning condenser.

Bureau of Standards,
Washington, D.C.,
June 25, 1921.

CIII. *On the Orbits in the Field of a Doublet.* *By* DOROTHY WRINCH, *Fellow of Girton College, Cambridge, and Member of the Research Staff, University College, London**.

Introductory.

THE present paper investigates in a somewhat systematic way the two-dimensional motion of a particle in the field due to a doublet. Several of the results are of course known already as isolated theorems, but the subject does not appear to have been treated by any writer in a comprehensive manner, and it is very difficult to obtain a general view of the motion of a particle around a doublet even in two dimensions by putting together the specific solutions found in dynamical treatises or memoirs. Some new results which may be of importance are arrived at in the present paper, for the doublet may be of many types: the analysis is equally appropriate to a magnetic pole moving under the influence of an elementary magnet or to an electric charge in the presence of an electric doublet. Physicists are now generally convinced that the structure of a neutral atom of an element follows the lines generally associated with the names of Rutherford and Bohr. Such an atom behaves towards an external electron sufficiently far away effectively like a doublet, and we have little knowledge of its capacity to attract and retain a stray electron and so form a negatively charged atom. In a vacuum tube, where the atoms are continually bombarded by electrons, we know that negatively charged atoms frequently occur; but the conditions conducive to the presence of a large number in cases in which their existence is chemically possible appear to be quite unknown.

The success of the quantum theory has generally established the fact that we must not expect to be able, by the use of classical dynamics, to determine the internal motions of the electrons actually constituting the atom; but if we recall the facts that

(*a*) the inverse square law of attraction between electric charges appears to remain valid at distances comparable with atomic dimensions,

(*b*) the essential need for the quantum type of dynamical specification only arises when an electron is "bound" or is already a constituent part of the atom,

we see that the motion of an external charge must, even

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* Communicated by the Author.

on this view, be governed by the formulæ of classical dynamics.

For these reasons the results of this paper should have some bearing on the conditions under which an electron originally moving in any way in the neighbourhood of an atom may be captured and retained. But in default of a more precise development of atomic theory, we have set out the results as solutions of a formal general dynamical problem in the theory of orbits, for the need for such a scheme of solution is recognized here as well as in electrical theory.

A doublet consisting of two equal and opposite charges—of electrical or other type—subject to the inverse square law of attraction admits a potential

$$V=-\mu\cos\theta/r^2$$

at all external points. This involves both a radial force R and a transverse force T on any unit particle in the field of the doublet. R is measured along r increasing, and T in the direction θ increasing. The values are given by

$$R=-\frac{\partial V}{\partial r}\qquad=-2\mu\cos\theta/r^3,$$

$$T=-\partial V/r\partial\theta=-\mu\sin\theta/r^3.$$

The equations of the orbit of the particle are of the well-known form

$$\ddot{r}-r\dot{\theta}^2\qquad=R,$$

$$1/r\,d/dt\,(r^2\dot{\theta})=T.$$

Denoting $r^2\dot{\theta}$ by h—so that mh is the angular momentum when the particle has mass m,—we can show that

$$h^2=(-R-T\,du/ud\theta)\;/\;h^2(u+d^2u/d\theta^2)$$

$$=\mu\,(\sin\theta\,du/d\theta+2u\cos\theta)\;/\;(u+d^2u/d\theta^2)\;;\qquad .\quad(1)$$

and also

$$dh^2/d\theta=2r^3T=-2\mu\sin\theta.\qquad .\;.\;.\;.\;.\quad(2)$$

These are obtained by the usual procedure of eliminating the time. The field of the doublet is symmetrical about the axis $\theta=0$, and we shall find it convenient to consider only those motions which begin on the side of the plane defined by

$$\pi\geq\theta\geq0\;;$$

for it is clear that other possible motions will merely be reflexions of these in the axis; their separate discussion is therefore unnecessary.

The equation may be integrated in the form

$$h^2 = 2\mu\,(\cos\theta - \cos\theta_1) + h_1^2,$$

where h takes the value h_1 when θ takes some specific value θ_1. Now motion can only take place when h is real, so that h^2 must not have negative values. It is therefore evident that no motion can occur when

$$2\mu\cos\theta_1 - h_1^2 > 2\mu,$$

and in the critical case,

$$2\mu\cos\theta_1 - h_1^2 = 2\mu,$$

the motion is restricted to the line $\theta=0$ and is given by

$$\ddot{r} = -2\mu/r^3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

Motion along the axis of the Doublet.

We may now proceed to discuss these motions along the axis in some detail.

The integrated form of the equation (1) is

$$\dot{r}^2 = C + 2\mu/r^2.$$

If the velocity U at the point of projection $r=r_1$ is $+U_1$, then

$$\frac{dr}{dt} = U = +\sqrt{U_1^2 + 2\mu/r^2 - 2\mu/r_1^2}.$$

If $U_1^2 > 2\mu/r_1^2$, the particle describes the line $\theta=0$ in the direction r increasing, with a steadily decreasing velocity. Its velocity at $r=\infty$ is $\sqrt{U_1^2 - 2\mu/r_1^2}$. Further, integrating the equation again, the time is given as a function of r in the form

$$t - t_1 = \left(\sqrt{(U_1^2 - 2\mu/r_1^2)r^2 + 2\mu} - \sqrt{2\mu}\right)/(U_1^2 - 2\mu/r_1^2),$$

and the time to infinity is infinite. Thus a particle with these conditions of projection will not leave the system in a finite time.

The case $U_1^2 = 2\mu/r_1^2$ gives a similar result. The particle describes the line $\theta=0$ in the direction r increasing with a steadily decreasing velocity, arriving there with zero velocity. The time is given by

$$t - t_1 = (r^2 - r_1^2)/2\sqrt{2\mu}\ ;$$

so that, as before, an infinite time is required for the description of the line $\theta=0$.

Now it may easily be seen that $+\sqrt{\frac{2\mu}{r_1^2}}$ is the smallest velocity of projection which causes a particle to recede from the doublet and ultimately to leave the system. When

$$U_1 < \sqrt{2\mu/r_1^2},$$

the particle returns to the doublet. For since

$$\dot{r} = U = \sqrt{(U_1^2 + 2\mu/r^2 - 2\mu/r_1^2)}, \quad . \quad . \quad . \quad (4)$$

U will vanish at $r = r_2$, where

$$1/r_1^2 - 1/r_2^2 = U_1^2/2\mu\,;$$

the particle then reverses its direction and approaches the doublet. Integrating equation (4), we have

$$t - t_1 = r_2\left(\sqrt{r_2^2 - r_1^2} - \sqrt{r_2^2 - r^2}\right)/\sqrt{2\mu}\,;$$

so that the time from $r = r_1$, at which $t = t_1$, to $r = r_2$, at which $t = t_2$, is

$$r_2\sqrt{r_2^2 - r_1^2}/\sqrt{2\mu}\,;$$

the particle reverses its direction, and its velocity is now given by

$$\dot{r} = -\sqrt{(2\mu/r^2 - 2\mu/r_2^2)},$$

and the time therefore by

$$t - t_2 = r_2\sqrt{r_2^2 - r^2}/\sqrt{2\mu}.$$

The time to the origin is consequently $r_2^2/\sqrt{2\mu}$. The particle therefore proceeds in the direction r increasing for a time $r_2\sqrt{r_2^2 - r_1^2}/\sqrt{2\mu}$, and then retraces its path, passing through its point of projection with a velocity equal to that with which it was projected and opposite in sign, arriving at the centre of force after a time

$$\left(r_2^2 + r_2\sqrt{r_2^2 - r_1^2}\right)/\sqrt{2\mu}$$

with infinite velocity.

Considering next the cases when the particle is projected towards the origin from $r = r_1$ with velocity U_1, we obtain the equation

$$\dot{r} = -\sqrt{U_1^2 + 2\mu/r^2 - 2\mu/r_1^2},$$

and whatever the magnitude of U_1 the particle goes to the origin with steadily increasing velocity and arrives there with an infinite velocity. The times can be obtained by integrating the equation in the form

$$t - t_1 = \frac{r_1}{U_1^2 r_1^2 - 2\mu}\left[U_1 r_1^2 - \sqrt{(U_1^2 r_1^2 - 2\mu) r^2 + 2\mu r_1^2}\right]$$

$$= \frac{r_1^2}{U_1 r_1^2 + \sqrt{2\mu r_1^2 + (U_1^2 r_1^2 - 2\mu) r^2}};$$

thus the time to the origin is

$$r_1/(U_1 + \sqrt{2\mu/r_1}),$$

giving $r_1/2U_1$ in the case when $U_1^2 = 2\mu/r_1^2$. The particle can consequently be sent to the origin in any time however small if U_1 is sufficiently large, and attain an infinite velocity in the time; it is further evident that it can approach the doublet with an infinite velocity even if it is projected with zero velocity or a velocity away from the origin, however small its original distance from the origin, provided only that it is not projected away from the doublet at the point r_1 with as great a velocity as $\sqrt{2\mu/r_1^2}$.

As regards motion on the line $\theta = \pi$, the equation is

$$\ddot{r} = 2\mu/r^3,$$

giving

$$\dot{r} = C - 2\mu/r^2.$$

Thus

$$\dot{r} = +\sqrt{U_1^2 - 2\mu/r^2 + 2\mu/r_1^2}$$

if U_1 is the velocity away from the origin at $r = r_1$. Thus $\dot{r}$ increases as r increases and has the value

$$\sqrt{U_1^2 + 2\mu/r_1^2}$$

at infinity. The time equation can be obtained as before, and it is found that the time of transit of the line is infinite. If, however, the particle is projected towards the origin

$$\dot{r} = -\sqrt{U_1^2 - 2\mu/r^2 + 2\mu/r_1^2}$$

and vanishes at $r = r_2$ given by

$$U_1^2 - 2\mu/r_2^2 + 2\mu/r_1^2 = 0;$$

the time to r_2 is

$$r_2\sqrt{r_1^2 - r_2^2}\,/\,\sqrt{2\mu},$$

and the particle recedes from the origin and disappears from the system, though only after an infinite time. Thus no conditions of projection in which U_1 is finite keep the particle from steadily increasing its distance from the doublet. If it is projected towards the doublet, it goes to the point $r=r_2$ and then recedes to infinity ; otherwise it moves away from it at once.

We have therefore two different types of motion, which are typical of the asymmetry of the field of force of the doublet. If the particle is in the line $\theta=\pi$, so long as the angular velocity is zero, no conditions of projection can prevent the particle from receding from the doublet with increasing speed, either immediately or after an interval

$$2r_2\sqrt{r_1^2-r_2^2}\,/\,\sqrt{2\mu}.$$

If, however, the particle is in the line $\theta=0$, so long as the angular velocity is zero, the particle does not leave the system unless projection is away from the origin and the velocity attains or exceeds the critical value $\sqrt{2\mu}\,/\,r_1$. If the velocity of projection away from the origin is less than $\sqrt{2\mu}\,/\,r_1$—and this includes the case of zero velocity or of projection towards the centre—the particle approaches the centre after an interval

$$2r_2\sqrt{r_2^2-r_1^2}\,/\,\sqrt{2\mu},$$

or directly, according as $U_1>0$ or $U_1\leq 0$, r_2 being given by

$$1/r_2^2 = 1/r_1^2-U_1^2/2\mu,$$

and the particle arrives at the centre in a finite time with infinite velocity.

These conclusions lead to curious effects of electrical doublets in the presence of stray electrons, which have apparently not been completely realized. It is remarkable that these stray electrons, when placed on one half of the axis of the doublet, should arrive from any distance, however large or small, and bombard the doublet with very great momentum ; and that, on the other hand, they must leave the system altogether if they are on the other side of the axis. It follows that a necessary consequence of the field of force created by a doublet is a continuous bombardment on one side by any stray electrons, and a steady ejection of electrons from the system on the other side.

General Motions.

Thus far, we have considered only the case when particles are projected from some point on the axes of symmetry of the doublet, with no angular velocity. The angular momentum is given, in general, by the equation

$$h^2 = h_1^2 + 2\mu(\cos\theta - \cos\theta_1) \; ; \quad . \quad . \quad . \quad . \quad . \quad (5)$$

so that if V be the transverse velocity at any point, and in particular V_1 the transverse velocity at (r_1, θ_1),

$$r^2V^2 = r_1^2V_1^2 + 2\mu(\cos\theta - \cos\theta_1).$$

Since h^2 cannot be negative, motion can only take place in the part of the plane in which

$$\cos\theta \geq \cos\theta_1 - h_1^2/2\mu.$$

It is now evident that there is an important division of the possible orbits in the field of the doublet. For if the initial conditions are such that

$$h_1^2 > 2\mu(1 + \cos\theta_1),$$

the condition that h^2 the square of the angular momentum is not negative is satisfied at all points of the plane, and the motion is therefore not restricted to any region of the plane, If, however,

$$-1 \leq \cos\theta_1 - h_1^2/2\mu = m \leq 1,$$

the expression for h^2 is positive or zero only when $\cos\theta - m$ is positive or zero ; and this plainly limits the motion to the sector of the plane (including the line $\theta = 0$) bounded by the radius vectors $\theta = \alpha$ and $\theta = -\alpha$, where $m = \cos\alpha$. Thus in this case, if $\cos\theta_1 - h_1^2/2\mu$ lies between zero and unity, the motion is restricted to the sector $\theta = \pm\alpha$, and α is not greater than $\pi/2$. If $h_1^2/2\mu - \cos\theta_1$ lies between zero and unity, the motion is restricted to a sector $\theta = \pm\alpha$, and in this case α is not less than $\pi/2$.

The initial transverse velocity of projection therefore determines the orbits to this extent. If

$$r_1^2V_1^2/2\mu > 1 + \cos\theta_1,$$

motion is possible all over the plane; if, however,

$$r_1^2V_1^2/2\mu = \cos\theta_1 - m$$

and

$$-1 \leq m = \cos\alpha \leq 1,$$

the motion is restricted to a sector $\theta = \pm\alpha$. Plainly, the larger $r_1^2V_1^2$ is, the larger is the sector ; in the limiting case when $r_1^2V_1^2/2\mu = 1 + \cos\theta_1$, the sector is the whole plane.

This discussion exhausts all possible cases, since plainly we cannot have

$$r_1^2V_1^2/2\mu < \cos\theta - 1.$$

Characteristics of the Radial Motion: Reduction to the Case of Motion on the Axis of the Doublet.

Consider next the (r, t) equation relating the radius vector to the time. We have

$$\ddot{r}-r\dot{\theta}^2=\ddot{r}-h^2/r^3=-2\mu\cos\theta/r^3.$$

Consequently,

$$\ddot{r}=-2\mu m/r^3,$$

where

$$m=\cos\theta_1-h_1{}^2/2\mu$$

as before. Now, we have already discussed the equations

$$\ddot{r}=-2\mu/r^3, \qquad \ddot{r}=+2\mu/r^3,$$

which give the motion on the lines $\theta=0$ and $\theta=\pi$ respectively in the case when the particle has no angular momentum. The results in two cases can be readily modified so as to cover the general case of motion—the first equation for the case when m is positive, and the second for the case when m is negative—by merely writing $2\mu m$ for 2μ. In fact, so far as the behaviour of r is concerned, the characteristics of orbits in which

$$0\geq r_1{}^2\mathrm{V}_1{}^2/2\mu-\cos\theta_1\geq-1$$

are similar to those on the line $\theta=0$; and the characteristics of orbits in which

$$r_1{}^2\mathrm{V}_1{}^2/2\mu-\cos\theta_1>0$$

are similar to those on the line $\theta=\pi$.

Thus, in the first set of cases, no conditions of projection with respect to the radial velocity can prevent the particle, either immediately or after a finite interval, receding from the origin with an ever-increasing velocity. In the second set of cases, it is only when the radial velocity is sufficiently big, viz.

$$\mathrm{U}_1\geq+\sqrt{2\mu m/r_1{}^2},$$

that the particle leaves the system. In all other cases the particle arrives at the doublet in a finite time with an infinite velocity.

The difference in the characteristics of these two classes of orbits is of course not unexpected. For when $|\theta|>\pi/2$ the radial force is repulsive, and for $|\theta|<\pi/2$ attractive. On $|\theta|=\pi/2$, it is zero. Consequently, if the particle has sufficient angular momentum to pass the line $|\theta|=\pi/2$, and not sufficient to regain the sector $|\theta|\leq\pi/2$ after one or more revolutions, nothing can prevent it from receding from the doublet, however great its initial radial velocity towards the doublet may be. If, however, the angular momentum is not great enough to enable the particle to get beyond the lines $|\theta| = \pi/2$, or is great enough to enable it to regain the sector $|\theta| \leq \pi/2$, it is only in the case of a sufficiently large radial velocity away from the origin that the particle can be prevented from approaching the centre (possibly after an excursion away from it finite in time and extent) and bombarding the doublet with an infinite momentum after a finite time.

Characteristics of the Orbits which lie in a Sector of the Plane.

We may now discuss the variation in V, the transverse velocity.

Suppose, first, that we limit ourselves to the cases when

$$0 \leq \cos\theta_1 - r_1^2 V_1^2/2\mu = \cos\alpha = m \leq 1,$$

in which the motion is restricted between the lines $\theta = \pm\alpha$ and $\alpha \leq \pi/2$.

V is always zero at all points of these bounding rays. Hence, except when U the radial velocity also happens to vanish at a point on the bounding rays, at such a point the velocity of the particle is entirely along the radius vector. Consequently at such a point the orbit touches the bounding rays, except in the special case when the radial velocity is also momentarily evanescent.

Motion therefore takes place in general along a curve of wave form touching alternately the bounding rays $\theta = \pm\alpha$. If the particle is projected at $r_1\theta_1$ with velocities $U = U_1 \geq 0$, $V = V_1$, the particle initially recedes from the doublet, touching the bounding rays alternately. If

$$U_1 \geq \sqrt{(2\mu\cos\alpha/r_1^2)}$$

it gets perpetually further from the origin. If, however,

$$V_1 < \sqrt{(2\mu\cos\alpha/r_1^2)}$$

the particle recedes from the origin along a curve of wave form, touching the rays alternately until it reaches a point r_2 given by

$$1/r_1^2 - 1/r_2^2 = U_1^2/2\mu\cos\alpha.$$

At this point its velocity along the radius vector is zero, and it therefore touches the circle $r = r_2$. Subsequently it approaches the doublet, converging on it along a wave-like path. In the case of an orbit of this type, the particle approaches the doublet with infinite velocity.

The equations of the orbits in these cases can be obtained either by integrating the original equation (1), which with the help of equation (2) may be written

$$2(\cos\theta-\cos\alpha)\,d^2u/d\theta^2-\sin\theta\,du/d\theta-2u\cos\alpha=0$$

or

$$\sqrt{(\cos\theta-\cos\alpha)}\frac{d}{d\theta}\left(\sqrt{(\cos\theta-\cos\alpha)}\frac{du}{d\theta}\right)-u\cos\alpha=0,$$

or we may obtain them by using the fact that $U/V=dr/rd\theta$. Proceeding from this, we obtain

$$-du/ud\theta=dr/rd\theta=\dot{r}/r\dot{\theta}=\pm\frac{\sqrt{(u^2-u_1{}^2+U_1{}^2/2\mu\cos\alpha)}}{u\sqrt{(\cos\theta/\cos\alpha-1)}}.$$

Hence

$$\frac{du}{\sqrt{U_1{}^2+2\mu u_1{}^2-2\mu u_1{}^2\cos\alpha}}=\pm\frac{d\theta}{\sqrt{2\mu}\sqrt{\cos\theta-\cos\alpha}}.$$

Now if the orbit is being described initially with r and θ increasing, $U/V>0$. This case needs the lower sign in the above equation.

Put

$$\sin\theta/2=\sin\alpha/2\,\mathrm{sn}\,(\psi,\sin\alpha/2),$$

where sn is the Jacobian elliptic function with modulus $\sin\alpha/2$, and we obtain

$$-\frac{d\theta}{\sqrt{2\mu}\sqrt{\cos\theta-\cos\alpha}}=-\frac{\sqrt{2}d\psi}{\sqrt{2\mu}}.$$

Further, putting

$$u=\sqrt{U_1{}^2/2\mu\cos\alpha-u_1{}^2}\sinh\xi,$$

we have

$$\frac{du}{\sqrt{U_1{}^2+2\mu u^2-2\mu u_1{}^2\cos\alpha}}=\frac{d\xi}{\sqrt{2\mu\cos\alpha}}.$$

Hence

$$\frac{\xi-\xi_0}{\sqrt{\cos\alpha}}=-\sqrt{2}\psi,$$

where ξ_0 is some constant; and we obtain the equation of the orbit in terms of a parameter ξ and constants α, ξ_0 in the form

$$\sin\theta/2=\sin(\alpha/2)\,\mathrm{sn}\left[(\xi_0-\xi)/\sqrt{2\cos\alpha},\sin\alpha/2\right],$$
$$u=\sqrt{(U_1{}^2/2\mu\cos\alpha-u_1{}^2)}\sinh\xi,$$

or writing $\xi_0 - \xi = \chi$,

$$\sin \theta/2 = \sin (\alpha/2) \operatorname{sn} (\chi/\sqrt{2 \cos \alpha}, \sin \alpha/2),$$

$$u = \sqrt{\mathrm{U}_1^2/2\mu \cos \alpha - u_1^2} \sinh (\xi_0 - \chi).$$

This curve consists of a series of waves touching $\theta = \pm \alpha$ alternately and going to infinity along the line

$$\chi = \xi_0, \qquad p = \left(-\frac{du}{d\theta}\right)_{u=0} = 0,$$

$$\theta = \theta_0, \qquad p = \left(-\frac{du}{d\theta}\right)_{u=0} = 0,$$

given by

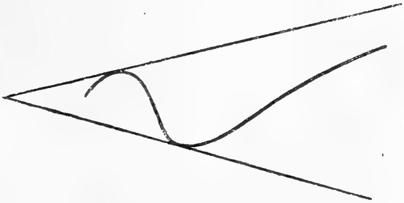
$$\sin \theta_0/2 = \sin \alpha/2 \operatorname{sn} \left[\xi_0 / \sqrt{2 \cos \alpha}, \sin \alpha/2\right].$$

To obtain ξ_0 in terms of the velocities of projection $\mathrm{U}_1 \mathrm{V}_1$ and the coordinates of the point of the projection $r_1 \theta_1$, we may remark that, if $\chi = \chi_1$, when $\theta = \theta_1$,

$$\sin \theta_1/2 = \sin \alpha/2 \operatorname{sn} (\psi_1 / \sqrt{2 \cos \alpha}, \sin \alpha/2),$$

$$\tanh \overline{\xi_0 - \chi_1} = u_1 \sqrt{2\mu \cos \alpha}/\mathrm{U}_1.$$

Fig. 1.



Thus

$$\xi_0 = \sqrt{2 \cos \alpha} \operatorname{sn}^{-1} (\sin \theta_1/2 / \sin \alpha/2)$$
$$+ \tanh^{-1} u_1 \sqrt{2\mu \cos \alpha}/\mathrm{U}_1 ;$$

and hence the direction $\theta = \theta_0$ is given by

$$\sin \theta_0/2 = \sin \alpha/2 \operatorname{sn} \left[\operatorname{sn}^{-1} (\sin \theta_1/2 / \sin \alpha/2) + \frac{1}{\sqrt{2 \cos \alpha}} \tanh^{-1} u_1 \sqrt{2\mu \cos \alpha} / \mathrm{U}_1 \right].$$

A typical curve of this class is shown in fig. 1.

In the case when $U_1^2/2\mu m = v_1^2$, the equation stands in the form

$$\frac{du}{u\sqrt{\cos\alpha}} = -\frac{d\theta}{\sqrt{\cos\theta-\cos\alpha}},$$

and we get

$$\frac{1}{\sqrt{\cos\alpha}}\log u/u_1 = -\sqrt{2}(\psi-\psi_1)$$

if $u=u_1$ when $\psi=\psi_1$, where

$$\sin\theta/2 = \sin\alpha/2 \operatorname{sn}(\psi, \sin\alpha/2)$$

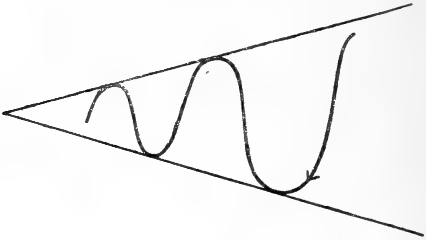
or

$$\sin\theta/2 = \sin\alpha/2 \operatorname{sn}\left[\frac{1}{\sqrt{2\cos\alpha}}\log u_1/u+\psi_1\right]$$

$$= \sin\alpha/2 \operatorname{sn}\left[\psi_1+\frac{1}{\sqrt{2\cos\alpha}}\log r_1/r\right].$$

This curve oscillates between $\theta=\pm\alpha$, with r continually increasing. As $r\to\infty$ θ is indeterminate, and instead of tending to infinity along a certain line $\theta=\theta_0$ after a finite number of contacts with the lines α and $-c$, as in the previous case when $U_1^2/2\mu\cos\alpha>v_1^2$, this curve oscillates between the rays $\pm\alpha$ and has no direction at infinity. A typical curve of this type is shown in fig. 2.

Fig. 2.



The case when $u_1^2-U_1^2/2\mu m = u_2^2 > 0$ remains. We have

$$\frac{du}{\sqrt{\cos a}\sqrt{u^2-u_2^2}} = -\frac{d\theta}{\sqrt{\cos\theta-\cos\alpha}}.$$

Putting $u=u_2\cosh\xi$, we get

$$\frac{du}{\sqrt{u^2-u_2^2}} = d\xi\,;$$

and consequently, if

$$\sin\theta/2 = \sin\alpha/2 \operatorname{sn}(\psi, \sin\alpha/2)$$

as before,

$$\xi-\xi_0 = -\sqrt{2\cos\alpha}\;\psi$$

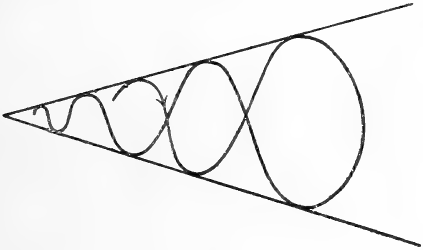
and the orbit in terms of a parameter ψ and constants ξ_0 and α is

$$\sin\theta/2 = \sin(\alpha/2)\,\mathrm{sn}\,(\psi, \sin\alpha/2),$$

$$u = \sqrt{u_1^2-\mathrm{U}_1^2/2\mu\cos\alpha}\,\cosh\left(\xi_0-\psi/\sqrt{2\cos\alpha}\right).$$

It is evident that in this case, as ψ increases from an initial value ψ_1, u decreases until $\psi=\xi_0/\sqrt{2\cos\alpha}$: it then increases to infinity; while at the same time θ is going from the value θ_1 through the cycle of values $(\alpha, 0, -\alpha, 0)$. A typical orbit of this kind is shown in fig. 3.

Fig. 3.



It is of interest to connect the constants in these equations with the constants given in the initial velocities at the point $r_1\theta_1$. We have, of course,

$$\mathrm{V}_1^2 = 2\mu u_1^2(\cos\theta_1-\cos\alpha),$$

which gives α in terms of v_1 θ_1 and V_1. Since $\theta=\theta_1$ when $r=r_1$, ξ_0 is given by the equations

$$\sin\theta_1/2 = \sin\alpha/2\,\mathrm{sn}\left(\chi_1/\sqrt{2\cos\alpha}, \sin\alpha/2\right),$$

$$\tanh\overline{\xi_0-\chi_1} = \mathrm{V}_1/\sqrt{2\mu u_1};$$

so that

$$\xi_0 = \sqrt{2\cos\alpha}\,\mathrm{sn}^{-1}\left(\sin\theta_1/2\,/\sin\alpha/2\right)$$

$$+\tanh^{-1}\mathrm{U}_1/\sqrt{2\mu u_1}\,\sqrt{\cos\alpha}.$$

It is perhaps hardly necessary to get the equation in the case of projection towards the origin, since the analysis is entirely similar to that required in the cases when projection is along the axis, and the geometrical characteristics of the curves obtained have already been indicated in the diagram. For example, the part of the curve (fig. 3) in which the particle is approaching the origin is a typical curve of the case when projection is towards the doublet.

Motions which are restricted to half the Plane, including one Periodic Orbit.

We have now considered the cases when

$$0 \leq 2\mu \cos \theta_1 - h^2 \leq 1.$$

We have considered in detail the boundary case

$$2\mu \cos \theta_1 - h_1{}^2 = 0,$$

in which motion is restricted to the line $\theta = 0$.

The particular features of the case

$$2\mu \cos \theta_1 - h^2 = 0, \qquad h^2 = 2\mu \cos \theta,$$

also call for attention. Here the motion is restricted to the positive side of the plane, given by

$$-\frac{\pi}{2} \leq \theta \leq \frac{\pi}{2}.$$

Referring to the equation

$$\ddot{r} - r\theta^2 = \mathrm{R},$$

we get in this case

$$\ddot{r} = 0, \qquad \dot{r} = \mathrm{U}_1;$$

so that the radial velocity is constant. Given then an outward radial velocity initially, the curve touches the lines $\pm\pi/2$ alternately, and the distance at any time from the origin of a particle describing it is given by

$$r - r_1 = \mathrm{U}_1(t - t_1)$$

if it is projected from r_1 with radial velocity U_1 at t_1. If $\dot{r} = -\mathrm{U}_1$, the particle approaches the doublet with constant radial velocity along a wave path which alternately grazes $\theta = \pm\pi/2$.

The equation to the orbit if $\dot{r} = \mathrm{U}_1 > 0$ results from the equation

$$-du/ud\theta = dr/rd\theta = \mathrm{U}_1/r\dot{\theta} = \frac{\mathrm{U}_1}{u\sqrt{2\mu}\sqrt{\cos\theta}}$$

or

$$du/d\theta = -\frac{\mathrm{U}_1}{\sqrt{2\mu}} \Big/ \sqrt{\cos\theta}$$

in the form

$$\sin\theta/2 = \frac{1}{\sqrt{2}} \operatorname{sn}(\psi, 1/\sqrt{2}),$$

$$u - u_1 = -\frac{\mathrm{U}_1}{\sqrt{2\mu}} \cdot \sqrt{2}\,(\psi - \psi_1)$$

if $u=u_1$ when $\psi=\psi_1$. Thus

$$\sin\theta/2 = 1/\sqrt{2}\,\mathrm{sn}\left[\psi_1-\frac{\mathrm{U}_1}{\sqrt{\mu}}(u-u_1)\right]$$

and

$$\sin\theta_1/2 = 1/\sqrt{2}\,\mathrm{sn}\,\psi_1.$$

The equation connecting θ and t can easily be obtained in the form

$$\sin\theta/2=1/\sqrt{2}\,\mathrm{sn}\left[\mathrm{sn}^{-1}(\sqrt{2}\sin\theta_1/2)+\frac{\mathrm{U}_1^2}{\sqrt{\mu}}\cdot\frac{(t-t_1)}{r_1(r_1+\mathrm{U}_1\overline{t-t_1})}\right].$$

In the case of $\dot{r}$ being negative originally and equal to $-\mathrm{U}_1$, we have

$$r-r_1 = \mathrm{U}_1(t_1-t),$$

and progress is towards the origin along a curve waving between $\theta=\pm\pi/2$ and cutting the line $\theta=0$ between each two consecutive grazings of these boundary lines. It may possibly be of interest to remark that the reciprocals of the distances of the various points on the rays $\theta=\alpha$, $\theta=0$, or $\theta=-\alpha$ are in arithmetic progression with common difference $\sqrt{2\mu}\,\mathrm{K}\,1/\sqrt{2}/u_1$.

A case of special interest occurs, however, when the radial velocity originally is zero. The curve will then be merely the part of the circle $r=r_1$ for which

$$-\pi/2 \leq \theta \leq \pi/2.$$

The transverse velocity is given by

$$\mathrm{V}^2 = 2\mu\cos\theta/r^2.$$

Thus, if a particle is given a transverse velocity

$$\mathrm{V}_1 = \sqrt{2\mu\cos\theta_1}/r_1$$

at the point $\theta_1 r_1$ and no radial velocity, it will describe the semicircle $r=r_1$, $|\theta|\leq\pi/2$ perpetually.

The periodic time is easily given by

$$\tfrac{1}{4}\mathrm{T} = \int_0^{\pi/2} r_1\frac{d\theta}{\mathrm{V}} = \frac{r_1^2}{\sqrt{2\mu}}\int_0^{\pi/2}\frac{d\theta}{\sqrt{\cos\theta}}$$

$$= \frac{r_1^2}{\sqrt{2\mu}}\int_0^{\pi/2}\frac{d\theta}{\sqrt{1-2\sin^2\theta/2}} = \frac{r_1^2}{\sqrt{2\mu}}\mathrm{K}(\sqrt{2})$$

$$= \frac{r_1^2}{\sqrt{2\mu}}\cdot\sqrt{2}\,\mathrm{K}(1/\sqrt{2}).$$

We have now, therefore, established the existence of a periodic orbit in the field of force

$$V = -\mu u^2 \cos\theta,$$

viz. the semicircle $r = r_1$, in which the periodic time is $4r_1^2 K(1/\sqrt{2})/\sqrt{\mu}$. The path of a particle is therefore this periodic orbit when the conditions of projection at $r_1\theta_1$ give

$$U_1 = 0, \qquad r_1^2 V_1^2 = 2\mu\cos\theta_1,$$

and only under these conditions.

It is further possible to deduce from our general analysis that when the transverse velocity of projection satisfies the conditions

$$0 \leq 2\mu\cos\theta_1 - r_1^2 V_1^2 \leq 2\mu$$

this semicircular path is the only periodic orbit possible.

We next consider the case when

$$0 < h_1^2 - 2\mu\cos\theta_1 \leq 2\mu.$$

Putting

$$h_1^2 - 2\mu\cos\theta_1 = -2\mu\cos\alpha = 2\mu m > 0,$$

we see at once that motion must be restricted to the sector

$$-\alpha \leq \theta \leq \alpha,$$

in which $\alpha > \pi/2$. In this case the (r, t) equation is

$$\ddot{r} = 2\mu m/r^3,$$

giving

$$\dot{r}^2 = U_1^2 + 2\mu m/r_1^2 - 2\mu m/r^2.$$

If $\dot{r}$ is originally positive or zero, $\dot{r}$ increases steadily to the value $\sqrt{(U_1^2 + 2\mu m/r_1^2)}$ at infinity; while if it is originally negative, it decreases in absolute magnitude until $r = r_2$, where

$$1/r_2^2 = 1/r_2^2 + U_1^2/2\mu m,$$

and then changes sign and increases steadily. We may integrate the equation in the form

$$t - t_1 = r_2(\sqrt{r_1^2 - r_2^2} - \sqrt{r^2 - r_2^2})/\sqrt{2\mu m} \text{ when } U_1 < 0,$$

and in the form

$$t - t_1 = r_2\sqrt{r^2 - r_2^2}/\sqrt{2\mu m} \quad \text{if } U_1 > 0.$$

Whatever, then, the initial radial velocity the particle proceeds either directly or after an interval

$$2r_2\sqrt{r_1^2 - r_2^2}/\sqrt{2\mu m}$$

to increase its distance from the origin at an increasing rate.

At the same time, the variation of θ can be obtained from the equations

$$\sin\theta/2 = \sqrt{\frac{m+1}{2}}\,\mathrm{sn}\left(\phi, \sqrt{\frac{m+1}{2}}\right)$$

$$r = r_1 \sec\left(\sqrt{2m}(\phi-\phi_1)\right),$$

or if the relation between θ and t is more convenient, from the equation

$$t-t_1 = (r_1^2/\sqrt{2\mu m})\tan\left(\sqrt{2m}\,(\phi-\phi_1)\right).$$

These equations can be deduced from the relation

$$\mathrm{U/V} = r d\theta/dr$$

as before. The path therefore, in general, waves backwards and forwards between $\theta = \pm\alpha$ a finite number of times (which may be zero), and has the asymptote

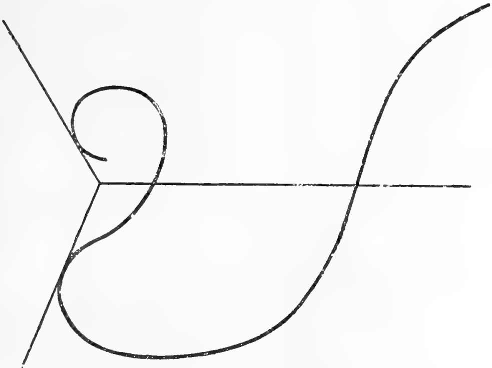
$$\theta = \theta_0, \quad p = (-du/d\theta)_{u=0},$$

given by

$$\sin\theta_0/2 = \sqrt{\frac{m+1}{2}}\,\mathrm{sn}(\phi_1 + \pi/2\sqrt{2m}).$$

A typical orbit is appended in fig. 4.

Fig. 4.



There is, however, one particular case. If

$$h_1^2 - 2\mu\cos\theta_1 = 2\mu,$$

then $\alpha = \pi$ and the transverse velocity disappears when the line $\theta = \pi$ is reached. Unless therefore the particle goes off to infinity before reaching the line $\theta=\pi$, it will approach the line tangentially and pursue the path solely along this line.

Characteristics of Orbits not restricted to a Sector of the Plane.

The final case to be considered is when

$$h_1^2-2\mu\cos\theta_1=2\mu m>2\mu.$$

In this case, since

$$h^2=2\mu(m+\cos\theta)$$

and

$$V^2=2\mu(m+\cos\theta)/r^2,$$

the transverse velocity never vanishes in the finite part of the plane. The equation to the orbit in terms of a parameter ϕ is still given by

$$\sin\theta/2=\sqrt{\frac{m+1}{2}}\ \mathrm{sn}\left(\phi,\sqrt{\frac{m+1}{2}}\right),$$

which is now more conveniently put in the form

$$\sin\theta/2=\mathrm{sn}\left(\sqrt{\frac{m+1}{2}}\phi,\sqrt{\frac{2}{m+1}}\right),$$

and

$$r=r_1\sec\sqrt{2m}(\phi-\phi_1),$$
$$U=\sqrt{2\mu m}\sqrt{1/r_1^2-1/r^2+U_1^2/2\mu m}.$$

The particle goes to infinity, as before, arriving there with the velocity $\sqrt{2\mu m}\sqrt{1/r^2+U_1^2/2\mu m}$, and with $\sqrt{2m}(\phi-\phi_1)=\pi/2$. Now the equation giving θ in terms of ϕ will show what angular distance from θ_1 is described before the particle reaches infinity. It is evident that as m increases this angular distance increases, giving in the limiting case an infinite angular distance. The orbit therefore, in this general case, is a curve described with r and θ increasing together and circumscribing the origin an increasing number of times as m increases, and tending to infinity along the line $\theta=\theta_0$, $p=\left(-\frac{du}{d\theta}\right)_{u=0}$. In the limiting case when m is infinite, the path of the curve circumscribes the origin for ever, and only has the circle at infinity as asymptote.

If the particle is projected with negative or zero radial velocity, and the transverse velocity still satisfies the conditions

$$r_1^2 V_1^2 - 2\mu \cos\theta_1 > 2\mu,$$

the particle approaches the origin to a distance $r = r_2$ given by

$$1/r_2^2 = 1/r_1^2 + U_1^2/2\mu m$$

in times given by

$$t - t_1 = r_2\left(\sqrt{r_1^2 - r_2^2} - \sqrt{r^2 - r_2^2}\right) / \sqrt{2\mu m},$$

and then recedes from the origin according to the law

$$t - t_1 = r_2\sqrt{r^2 - r_2^2} / \sqrt{2\mu m}.$$

While the particle is first approaching and then receding from the origin, the variation of θ with t is given by

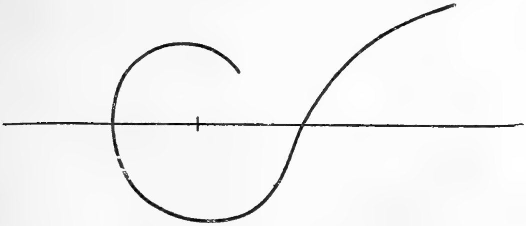
$$\sin\theta/2 = \operatorname{sn}\left(\sqrt{\frac{m+1}{2}}\,\phi,\ \sqrt{\frac{2}{m+1}}\right),$$

$$t - t_1 = r_1^2 / \sqrt{2\mu m} \tan \sqrt{2m}(\phi - \phi_1)\ ;$$

so that the orbit circumscribes the origin until that value of θ is reached for which $(\phi - \phi_1)\sqrt{2m} = \pi/2$.

A typical orbit is shown in fig. 5.

Fig. 5.



As in the previous cases, if the initial radial velocity is towards the origin there is a finite excursion towards the origin before the radial velocity becomes positive and increases steadily as time goes on.

Summary.

The general characteristics of the orbits in the field of a doublet may be summed up as follows :—

(*a*) The only periodic orbits are the semicircles

$$r = r_1, \qquad -\pi/2 \leq \theta \leq \pi/2,$$

for various values of r_1. The corresponding periodic time is

$$r_1^2\, K(1/\sqrt{2})/\sqrt{\mu}.$$

These orbits are described when and only when the conditions of projection at the point $(r_1\theta_1)$ are such that the radial velocity is zero and the transverse velocity V_1 is given by

$$r_1^2 V_1^2 = 2\mu \cos \theta_1.$$

Included under these conditions is the case when a particle is placed at rest on either of the lines $\theta=\pi/2$, $\theta=-\pi/2$, at any non-zero non-infinite distance r_1 from the doublet. The orbit will then be the appropriate semicircle, and the periodic time will be as above.

(*b*) When the transverse velocity of projection is such that

$$0 \leq 2\mu \cos \theta_1 - r_1^2 V_1^2 = 2\mu m \leq 2\mu,$$

the particle only leaves the system if U_1, the radial velocity, is greater than or equal to $\sqrt{2\mu m/r_1}$. The orbit touches the rays $\theta = \pm\alpha$ alternately, where $\cos\alpha = m$, and proceeds to infinity with a certain line

$$\theta = \theta_0, \quad p = (-dv/d\theta)_{u=0},$$

as asymptote, if $U_1 > \sqrt{2\mu m/r_1}$. If $U_1 = \sqrt{2\mu m/r_1}$, the orbit touches the rays alternately for ever and does not have a linear asymptote.

If, however, U_1 does not attain this critical velocity, the orbit touches the rays alternately and keeping to the sector $|\theta| \leq \alpha$, first recedes from the doublet if $U_1 > 0$, and then approaches the doublet converging on it, through a series of waves of decreasing amplitude, which touch the lines which bound it. If U_1 is negative, the orbit has similar characteristics, the excursion away from the origin being now deleted. However, whatever the value of U_1, under the condition

$$0 \leq 2\mu \cos \theta_1 - r_1^2 V_1^2 \leq 2\mu$$

the orbit is confined between the two rays $\theta = \pm\alpha$, where $\alpha \leq \pi/2$, and

$$2\mu \cos \theta_1 - r_1^2 V_1^2 = 2\mu \cos \alpha,$$

and is of wave form converging on or diverging from the doublet, the amplitude of the wave varying in such a way that the curve touches the lines which bound it.

(*c*) When the transverse velocity of projection is such that

$$0 < r_1^2 V_1^2 - 2\mu \cos \theta_1 \leq 2\mu,$$

the orbit, whatever U_1 may be, whether it is negative or positive, goes to infinity and the particle describing it recedes from the origin—after a finite excursion towards the doublet if U_1 is negative—at a steadily increasing rate, and it takes an infinite time to leave the system. The path again lies between bounding rays $\theta = \pm\alpha$, but

$$\cos\alpha = \cos\theta_1 - r_1^2 V_1^2/2\mu,$$

and therefore α is greater than $\pi/2$; the orbit is therefore confined to an oblique-angled sector of the plane. The path in general touches the bounding rays a finite number of times or not at all and has a certain straight line as asymptote. No velocity of projection towards the origin, however large, enables the particle to reach the doublet, or prevents it continually increasing its distance from the origin, possibly after it has approached within a certain distance of the doublet.

(*d*) When the transverse velocity is such that

$$2\mu < r_1^2/V_1^2 - 2\mu\cos\theta_1$$

the orbit is not restricted to any sector of the plane. The particle again approaches the doublet if the radial velocity of projection is towards the origin, but it never reaches it: in this case it ultimately recedes from the doublet. When the radial velocity of projection is positive it straightway recedes from the doublet. While the distance of the particle of the doublet is changing in this way, the angular distance of the particle from its initial position steadily increases, and it finally proceeds to infinity in the direction of a certain line, after a finite number of circumscribings of the origin. As

$$r_1^2 V_1 - 2\mu\cos\theta_1$$

increases, the orbit becomes more and more like the orbit in the limiting case when

$$r_1^2 V_1^2 - 2\mu\cos\theta_1$$

is infinite; in this case the particle circumscribes the doublet in the same sense, for ever, while its distance from the doublet increases without limit.

The main interest of the results lies probably in the electrification of neutral atoms in a vacuum tube—the neutral atom being taken, as usual, in its first approximation as a doublet. All the formulæ deduced involve, essentially, a critical velocity of an electron, which determines whether it leaves the atom in whose proximity it finds itself, or whether it stays. On the Quantum Theory, the criteria which determine the actual capture of such an electron by an atom have not yet been defined, and the fact that an electron "stays," according to this analysis, does not perhaps of itself involve its capture and retention as a constituent part of a negatively charged atom. Nevertheless there must be a correspondence and perhaps a rough proportionality between the two classes of phenomena—free electrons with a velocity distribution about the critical value, and the number of negatively charged atoms found in tubes under the conditions of discharge. It would seem that an experimental estimate of the number of such atoms is desirable in relation to the velocity distribution in the free electrons of which we have some definite knowledge. The Quantum Theory of atoms itself, proceeding as it does by the elaboration of successive hypotheses, still requires a hypothesis regarding the capture of electrons and the formation of negatively charged atoms. It would be of interest if it could be shown that a stray electron which by the foregoing analysis could not leave the system really became "bound" as a constituent part of the atomic: we may, indeed, perhaps anticipate that this phenomenon usually occurs.

CIV. *On a Simplified Proof for the Retarded Potentials and Huyghens's Principle.* *By* E. H. KENNARD, *Ph.D.**

THE proof usually given in deducing the retarded potentials and Huyghens's Principle seems to the author, as it must to many physicists, peculiarly abstract and indirect. This objection is only partly met in Professor Mason's † modification. The following proof seems to be at least as short and as rigorous as any other, while, at the same time, it seems more natural and easier for a physicist to follow.

§ 1. *New Proof.*

The scalar potential ϕ satisfies the differential equation

$$\frac{1}{c^2}\frac{\partial^2\phi}{\partial t^2}=\nabla^2\phi+4\pi\rho, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where ρ = density of electricity (the units being "ordinary").

To find ϕ at time t at any point P, let us surround P by any closed surface S and then, following Abraham, let us

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* Communicated by the Author.

† Max Mason, Phys. Rev. vol. xv. p. 312 (1920).

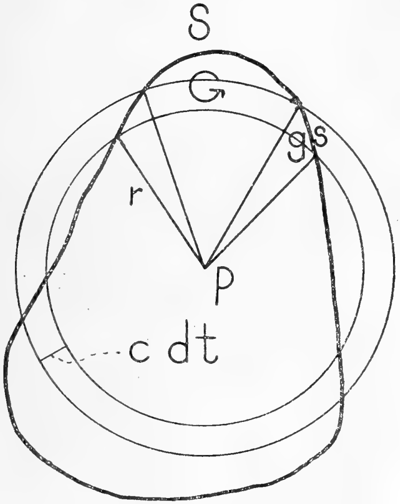
suppose a sphere with centre at P to contract with the speed of light so as to shrink to a point at P at time t.

Let us consider the integral

$$\mathrm{I}=\frac{1}{4\pi}\iint\left(\phi+r\frac{\partial\phi}{\partial r}+\frac{r}{c}\frac{\partial\phi}{\partial t}\right)d\omega, \quad . \quad . \quad . \quad (2)$$

where r = radius of the sphere, c = speed of light, ω = solid angle about P, and the surface of integration is the portion G of the sphere that is momentarily included within S.

Clearly at time t the last two terms become negligible (at least, provided the first derivatives of ϕ are all bounded or limited in value) and I reduces to the value of ϕ at P.



We can obtain a connexion between I and ρ by considering the change produced in I when the sphere contracts from one position to another through a distance $-dr = cdt$. The change in any term Z of the integrand is

$$\frac{\partial \mathrm{Z}}{\partial t}dt+\frac{\partial \mathrm{Z}}{\partial r}dr \text{ or } dt\left(\frac{\partial \mathrm{Z}}{\partial t}-c\frac{\partial \mathrm{Z}}{\partial r}\right).$$

Hence

$$d\mathrm{I}=\frac{dt}{4\pi}\iint_{\mathrm{G}}\left[-2c\frac{\partial\phi}{\partial r}-cr\frac{\partial^2\phi}{\partial r^2}+\frac{r}{c}\frac{\partial^2\phi}{\partial t^2}\right]d\omega$$
$$+\frac{1}{4\pi}\iint_{g}\left(\phi+r\frac{\partial\phi}{\partial r}+\frac{r}{c}\frac{\partial\phi}{\partial t}\right)d\omega, \quad . \quad . \quad (3)$$

the second integral extending only over the increment g which is added to G by the displacement of the sphere.

Now by (1)

$$\frac{dt}{4\pi}\iint\frac{r}{c}\frac{\partial^2\phi}{\partial t^2}d\omega=\frac{cdt}{4\pi r}\iint(\nabla^2\phi)r^2d\omega+\frac{cdt}{r}\iint\rho r^2d\omega\,. \qquad (4)$$

But $cdt\iint(\nabla^2\phi)r^2d\omega$ is, in the limit when $dt\doteq 0$, equal to the volume integral of $\nabla^2\phi$ throughout the shell bounded by the two limiting positions of the sphere and by the ring s which these cut out of S, and this volume integral in turn, by the divergence theorem (or "Green's theorem"), equals the outward normal flux of the vector $\nabla\phi$ over the surface of the shell. Hence we can write

$$\frac{cdt}{4\pi r}\iint_{G}(\nabla^2\phi)r^2d\omega=\frac{cdt}{4\pi r}\frac{\partial}{\partial r}\iint_{G}\frac{\partial\phi}{\partial r}r^2d\omega+\frac{1}{4\pi r}\iint_{g}\left(-\frac{\partial\phi}{\partial r}\right)r^2d\omega$$
$$-\frac{1}{4\pi r}\iint_{s}\frac{\partial\phi}{\partial n}dS, \quad . \; . \; . \; . \; . \; . \; . \; . \qquad (5)$$

where n = distance along inward normal to S.

Substituting from this equation in (4) and then from (4) back into (3), we find that many terms cancel out and

$$dI=cdt\iint_{G}\left(\frac{\rho}{r}\right)r^2d\omega+\frac{1}{4\pi}\iint_{g}\left(\phi+\frac{r}{c}\frac{\partial\phi}{\partial t}\right)d\omega-\frac{1}{4\pi}\iint_{s}\frac{1}{r}\frac{\partial\phi}{\partial n}dS$$
$$. \; . \; . \; . \; . \qquad (6)$$

Let us now write instead of $d\omega$ in the second integral, $dS\cos\theta/r^2$ where θ = angle between r drawn toward P and the inward normal to S; and let us write in place of the first term $\iiint(\rho/r)d\tau$ taken throughout the shell bounded by s and the two limiting positions of the sphere. We can then integrate and obtain I. At time $t=-\infty$, $I=0$; at time t, $I=\phi$, as noted above. Hence

$$\phi=\iiint\left[\frac{\rho}{r}\right]_{t-\frac{r}{c}}d\tau+\frac{1}{4\pi}\iint\left[\left(\frac{\phi}{r^2}+\frac{1}{cr}\frac{\partial\phi}{\partial t}\right)\cos\theta-\frac{1}{r}\frac{\partial\phi}{\partial n}\right]_{t-\frac{r}{c}}dS$$
$$. \; . \; . \; . \; . \qquad (7)$$

Here the first integral extends throughout all the space enclosed by S while the second extends over all of S, and the subscript reminds us that values of quantities inside the brackets are to be taken at a time $t-r/c$.

If we now let S recede to infinity, the surface integral may vanish : in that case we have the usual expression,

$$\phi=\iiint\left[\frac{\rho}{r}\right]_{t-\frac{r}{c}} d\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

the integral extending throughout all space.

In any case the surface integral expresses the effect at P of all electricity and all field conditions outside of S and constitutes the usual mathematical formulation of Huyghens's Principle.

The same proof applies at once, of course, to each component of the vector potential.

§ 2. *Heuristic Argument for the Student.*

This proof is particularly easy to lead up to. Electrostatic analogies suggest seeking a solution of (1) that will represent a train of spherical waves proceeding from a variable point-charge, and (8) is then easily guessed as the general solution (*cf.* Jeans, 'Electricity and Magnetism').

Abraham's contracting sphere is then introduced as a convenient way of visualizing the solution. It is next suggested, either on the basis of general reasoning or from the analogy of Green's stratum, that the contracting sphere ought to be able to obtain contributions of potential which shall represent the effect of conditions outside S from the elements of S itself. Finally, we note that the spherical wave from any element of charge which produces the contribution of this element at P at time t just keeps in contact with the sphere as the latter contracts, and we conclude that the contributions from all sources outside S must be capable of representation as an integral expressed in terms of the instantaneous field conditions over the sphere. The study of the integral I then falls naturally into place.

Even the form of I can, if desired, be heuristically obtained by proceeding from the analogy of the relationship between the mean electrostatic potential over a sphere and its value at the centre.

Physical Laboratory,
Cornell University.

CV. *On the Forced Vibrations of Bridges.*
By Professor S. P. TIMOSHENKO [*].

IT is now generally agreed that imperfect balance of the locomotive driving-wheels is the principal source of impact effect in bridges of long span. The laws governing this effect have not yet been definitely formulated, and much more information is needed on the experimental side [†].

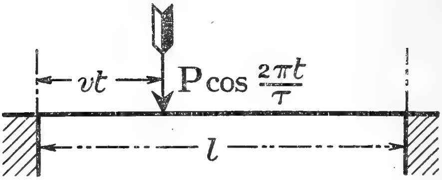
Some idea of the forced vibrations which are thus induced may be obtained by considering the bridge as a beam of constant cross-section with supported ends (fig. 1). The deflexion of the vibrating beam may be represented as follows :—

$$y=\phi_1 \sin\frac{\pi x}{l}+\phi_2 \sin\frac{2\pi x}{l}+\phi_3 \sin\frac{3\pi x}{l}+\ldots \quad . \quad . \quad (1)$$

where ϕ_1, ϕ_2, ..., etc. are functions of t only. Then if EI denotes the flexural rigidity of the beam, and w its weight per unit length, the expressions for the potential and kinetic energies will be

$$\left.\begin{aligned} V&=\frac{1}{2}\mathrm{EI}\int_0^l\left(\frac{\partial^2 y}{\partial x^2}\right)^2 dx=\frac{1}{4}\frac{\mathrm{EI}\pi^4}{l^3}\sum_{n=1}^{\infty}[n^4\phi_n{}^2], \\ T&=\frac{1}{2}\frac{w}{g}\int_0^l \dot{y}^2 dx=\frac{1}{4}\frac{wl}{g}\sum_{n=1}^{\infty}[\dot{\phi}_n{}^2]. \end{aligned}\right\} \quad . \quad (2)$$

Fig. 1.



We suppose that a single variable force P cos $2\pi t/\tau$ moves along the beam with a constant velocity v (fig. 1). The corresponding differential equations may be written in the form

$$\frac{wl}{2g}\ddot{\phi}_n+\frac{\mathrm{EI}\pi^4}{2l^3}n^4\phi_n=\mathrm{P}\cos\frac{2\pi t}{\tau}\sin\frac{n\pi vt}{l}. \quad . \quad . \quad (3)$$

Then taking $\phi_n=\dot{\phi}_n=0$ at the instant $t=0$, and writing

$$a^2=\frac{g\mathrm{EI}}{w},$$

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[*] Communicated by Mr. R. V. Southwell.

[†] *Cf.* 'Engineering,' vol. cxii. p. 80 (1921).

we obtain

$$\phi_n = \frac{l^2}{n^2\pi^2 a} \cdot \frac{2g}{wl} \int_0^t \mathrm{P} \cos\frac{2\pi t_1}{\tau} \sin\frac{n\pi v t_1}{l} \sin\frac{n^2\pi^2 a(t-t_1)}{l^2}\, dt_1, \qquad (4)$$

and the expression (1) may be written as follows :—

$$y = \frac{\mathrm{P}l^3}{\pi^4 \mathrm{EI}} \sum_{n=1}^{\infty} \left[\sin\frac{n\pi x}{l} \left\{ \frac{\sin\left(\frac{n\pi v}{l} + \frac{2\pi}{\tau}\right)t}{n^4 - (\beta + n\alpha)^2} + \frac{\sin\left(\frac{n\pi v}{l} - \frac{2\pi}{\tau}\right)t}{n^4 - (\beta - n\alpha)^2} \right.\right.$$
$$\left.\left. + \frac{\alpha}{n} \left(\frac{\sin\frac{n^2\pi^2 at}{l^2}}{n^2\alpha^2 - (n^2 - \beta)^2} + \frac{\sin\frac{n^2\pi^2 at}{l^2}}{n^2\alpha^2 - (n^2 + \beta)^2} \right) \right\} \right], \quad . \quad . \quad (5)$$

where $\alpha = \frac{vl}{a\pi}$; $\beta = \frac{2l^2}{\pi a \tau}$.

If the period τ of the force is the same as the period $\tau_1 \left(= \frac{2l^2}{\pi a}\right)$ of the principal mode of vibration of the beam, resonance will occur, and the amplitude of the forced vibration will increase with t. Under these conditions, we have

$$\beta = 1,$$

and at the instant when the periodic force ceases to act upon the bridge we have

$$t = l/v,$$

so that $\alpha = \frac{1}{2}\frac{\tau_1}{t}$ (in general, a small quantity).

Then the first term (for $n=1$) in the series on the right of (5), which is the most important part of y, may be reduced to the form

$$\frac{2\mathrm{P}l^3}{\pi^4 \mathrm{EI}} \sin\frac{\pi x}{l} \cdot \frac{1}{\alpha} \sin\frac{2\pi t}{\tau},$$

and the maximum value of the deflexion is given by the formula

$$f_{\max.} = \frac{2\mathrm{P}l^3}{\alpha\pi^4 \mathrm{EI}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Since, as we have seen, α is usually a small fraction, we may conclude from (6) that the forced vibration produced by want of balance in locomotives may be of practical importance.

The same method can be applied in other cases, where more complicated expressions are required for the forces which produce the vibration, and also in cases where variable horizontal forces act on the beam.

Zagreb, Yougoslavia.
Dec. 11th, 1921.

CVI. *The Occurrence of Ionization by Cumulative Effects.*
By FRANK HORTON *and* ANN CATHERINE DAVIES [*].

IN the Philosophical Magazine for March 1922, Professor K. T. Compton replies to criticisms we made [†] of the experiments by which he claims to have demonstrated the ionization of helium below its normal ionizing voltage, as the result of electron impacts against atoms which have absorbed resonance radiation from neighbouring atoms [‡]. In this reply Prof. Compton produces evidence which he states " proves these criticisms to be unfounded."

The experiments which we criticized as giving inconclusive results were made with an apparatus in which the collecting electrode was in the form of a hollow cylindrical box having one plane end of platinum gauze and the other plane end of platinum foil, arranged so that each end in turn could be faced towards the glowing filament. The ratio R of the currents measured in the two cases is $\frac{i+r}{i+cr}$, where i is the part of the measured current which is due to ionization (which is the same whichever end of the box faces the filament), and r and cr are the parts of the measured current which are due to the photoelectric effects of radiation when the foil end and the gauze end, respectively, face the filament. Hence, if the constant c is known, the ratio of i/r can be calculated from the ratio R of the two measured currents. For pure radiation the value of R is $1/c$, and for pure ionization it is unity. Prof. Compton assumed that the value of c was given by the ratio of the area covered by the wires of the gauze end to the total area of the plane end, and checked his calculation of this by comparing the photoelectric currents measured when using radiation from a quartz-mercury arc outside the apparatus. The value used by him in estimating i/r was 0·5. The following table, which is taken from Prof. Compton's paper, gives the values of R and i/r obtained for electron energies between 20 and 25 volts, at different pressures of helium:—

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[*] Communicated by the Authors.

[†] F. Horton and A. C. Davies, Phil. Mag. vol. xlii. p. 746 (1921).

[‡] K. T. Compton, Phil. Mag. vol. xl. p. 553 (1920).

p (mm.).	R.	i/r.
0·0005	1·90	0·055
0·001	1·81	0·116
0·003	1·74	0·176
0·012	1·60	0·333
0·015	1·57	0·378
0·044	1·55	0·410
0·17	1·40	0·75
1·00	1·19	2·22
8·00	1·07	6·3
25·00	1·04	11·4

In considering the origin of any ionization obtained below the normal ionizing voltage of helium under the conditions of his experiments, Prof. Compton dismisses the possibility of its being due to electron impacts against helium atoms in such rapid succession that the energies of the impacts are additive in their effect, for reasons given by him in another paper *. He explains the ionization by supposing that part of the necessary energy is acquired from the radiation produced at the minimum radiation voltage, which is assumed to be absorbed and re-emitted by other atoms and thus passed on from atom to atom. That this assumption is justified has been shown by recent experiments of the writers †. It is, however, upon this very property of the radiation (which is so essential to Prof. Compton's interpretation of his results) that the writers based their main criticism of his deduction that ionization of helium was occurring at all the pressures given in the table, and that the ratio of the ionization current to the radiation current at each pressure in his experiments is that stated in the third column.

Prof. Compton's criterion for the presence of ionization was the deviation of the experimentally determined value of the ratio R from the value which he took to be the standard one for a pure radiation effect, viz. $R=1/c=2$. Any error in the value taken as the standard seriously affects the interpretation of the experimental results, and it was pointed out in our criticism of these experiments that the occurrence of the process of the handing on of the helium radiation from atom to atom of necessity means that the area of the collecting electrode acted upon by the radiation in any given case is not simply the area of the covered part of the particular plane end of this electrode which is facing the filament, but may include also the area of the curved surface of the cylinder and possibly even the area of the plane end

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* K. T. Compton, Phys. Rev. vol. xv. p. 476 (1920).

† F. Horton and A. C. Davies, Phil. Mag. vol. xlii. p. 746 (1921).

remote from the filament. In his reply to this point Prof. Compton admits that some uncertainty exists in the value of R which can be taken as denoting a pure radiation effect, but asserts that the observed variation in R with variation of the pressure of helium is entirely too large to be accounted for in this way, quoting as an instance the result he obtained at 25 mm. pressure. It follows, from the additional data now given by Prof. Compton, that in the case of eight out of the ten results in his table (quoted above) the observed variation in R is not such as to justify the statement that it cannot be adequately accounted for without assuming the presence of ionization.

The area of the cylindrical surface of the collecting electrode is stated to have been equal to four times the area of the plane end of this electrode. Hence the limiting value of R for pure radiation, a value to which R will approximate when the radiation is so scattered by repeated absorption and re-emission that it is as likely to fall on the curved surface as upon the front plane end, would be $\frac{4r+r}{4r+0{\cdot}5r}=1{\cdot}11$, where r is, as before, the photoelectric current from the foil-covered plane end of the collecting electrode. In deducing this limiting value of R for pure radiation we have neglected the photoelectric effect from the plane end of the collecting electrode remote from the filament, as this is unfavourably situated in regard to the electric field, whereas the cylindrical surface is, according to the diagram of the apparatus, in a situation comparable with that of the front plane end so far as this field is concerned.

At very low pressures the radiation cannot suffer much deviation from its original direction through absorption and re-emission by helium atoms, and hence the front plane end of the collecting electrode will, in these cases, receive nearly all of the radiation which falls on the outside of this electrode, and the value of R will approximate to the value 2 assumed by Prof. Compton. At higher pressures, however, the curved surface receives a larger proportion of the total radiation falling on the collecting electrode, and hence, as the pressure is increased, R decreases from the value 2 and approaches more and more nearly to the limiting value 1·11. From the table already quoted, it will be seen that the decrease in the experimental value of R with increase of the pressure of helium is such as might be anticipated for a pure radiation effect, and that only in the two cases in which the pressure was very considerable do the experimental values of R fall below the limiting value for pure radiation. Thus in eight out of the ten instances the experiments do not give conclusive evidence of the presence of ionization below the normal ionizing voltage of helium.

There is, of course, ample evidence from spectroscopic observations * that when the pressure of the gas is considerable, ionization, which is presumably produced by cumulative action, occurs below the normal ionizing voltage, but this does not show, as Prof. Compton implies in his recent paper, that the results of the experiments we have criticized are reliable.

In regard to our criticism of Prof. Compton's original contention that the neon which was present in the helium used in his earlier experiments would be incapable of causing the effects he obtained at different pressures, it must be pointed out that the interesting new evidence of the purity of the helium used in the later experiments does not affect our objection to his original contention.

CVII. *On the Buckling of Deep Beams.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN connexion with the two papers on the Buckling of Deep Beams published in your periodical (see Dr. J. Prescott, xxxvi. p. 297 and xxxix. p. 194), I beg to communicate the following:—

The question of the buckling of beams can be regarded as solved for a long time already. The first paper on this subject was published in your periodical by A. G. M. Michell, 1899, vol. xlviii. The same problem was investigated with more details by Prof. L. Prandtl, 1899 (*Munich Dissert.*). In both these papers, as also in the paper of Dr. J. Prescott, the bending of the flanges of girders by sideways buckling is neglected, and in consequence of that the results cannot be applied to the calculation of I girders.

The influence of the flexion of flanges of the girder was studied by me, and the results were published in Russia, 1905 (Bulletins of the Polytechnical Institute, Petersburg).

The translation of this paper in German can be found in *Zeitschr. f. Math. u. Phys.*, Bd. lviii. (1910). Other manner of

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* O. W. Richardson and C. B. Bazzoni, Phil. Mag. vol. xxxiv. p. 285 (1917); K. T. Compton, E. G. Lilly, and P. S. Olmstead, Phys. Rev. vol. xvi. p. 282 (1920); A. C. Davies, Proc. Roy. Soc. A, vol. c. p. 599 (1922).

solution is given in my memoir published in French (*Annales des ponts et chaussées*, 1913, Fasc. iii.–v.). There are given the numerical tables, which enable us to calculate very easily I girders under different conditions of loading and fastening of the ends.

Yours truly,
S. TIMOSHENKO.

70 Sinclair Rd., W. 17.
August 30, 1921.

CVIII. *Notes on the Measurement of Absolute Viscosity.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,

SINCE the publication of my paper "Notes on the Measurement of Absolute Viscosity" in the February number of this Magazine, my attention has been drawn to the fact that the variable head correction had already been noticed by Meissner (*Chem. Rev. über die Fett & Hartz Industrie*, vol. xvii. p. 202, 1910), by Simeon (Phil. Mag. xxvii. p. 38, 1914), and by Bingham, Schlessinger, and Coleman (Journ. Amer. Chem. Soc. 1916, p. 27); also the value of unity for the kinetic energy coefficient was found by Couette and Finkener, and again by Kohlrausch (*Lehrbuch der Praktischen Physik*, p. 258, 11th edition, 1910).

I can only say that for my own part the work in my paper was entirely original, and I had no idea the ground had been covered before, all of which, of course, only serves to emphasize the necessity of keeping in touch with current literature.

Yours faithfully,
FRANK M. LIDSTONE.

Derby, March 31st, 1922.

CIX. *Intelligence and Miscellaneous Articles.*

ON THE MEASUREMENT OF ABSOLUTE VISCOSITY.

To the Editors of the Philosophical Magazine.

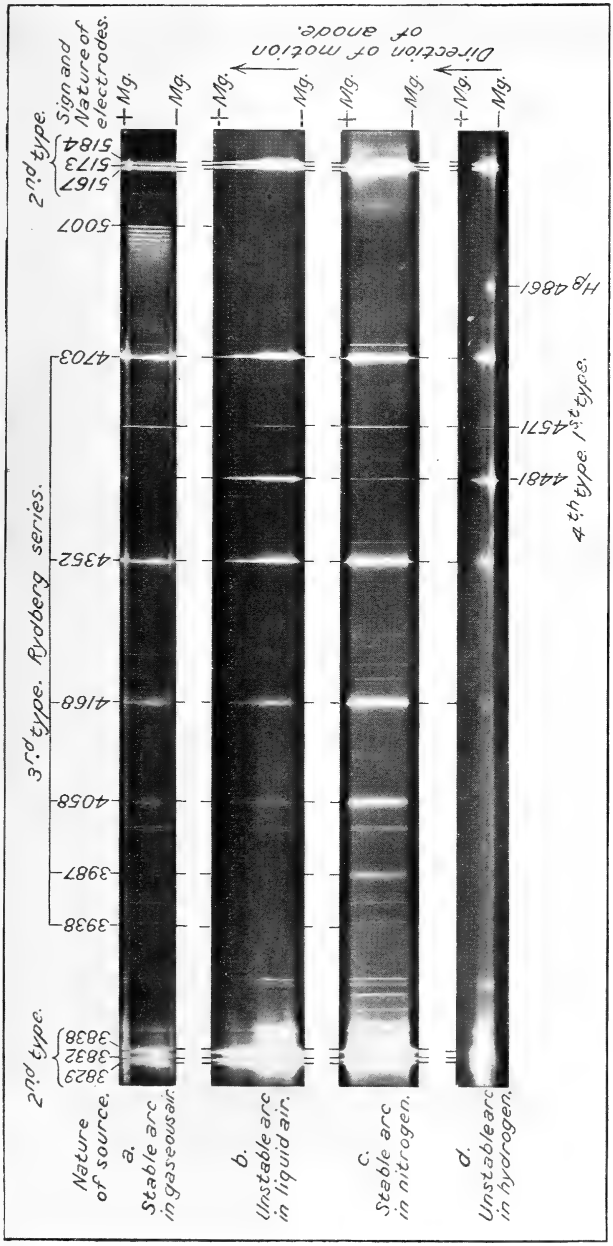
DEAR SIRS,—

MAY I point out with reference to the paper by Mr. Lidstone in the February number of the Philosophical Magazine, p. 354, that the equation deduced there for the viscosity of a liquid can only be used if the flow is from a uniform tube on the "high" side of the capillary tube to a uniform tube (not necessarily of the same bore as the other uniform tube) on the "low" side of the capillary tube.

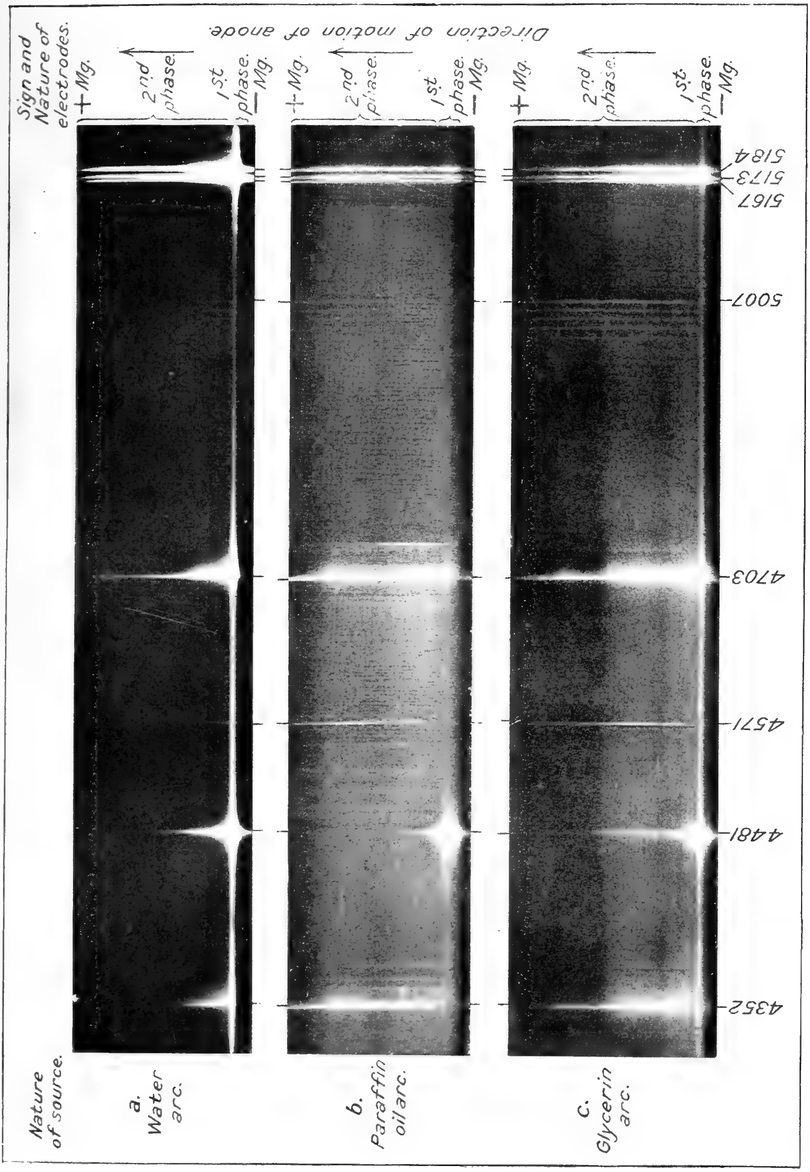
I am,
Yours truly,
JOHN SATTERLY.

University of Toronto,
Physics Dept.
April 7, 1922.

HEMSALECH & DE GRAMONT. Phil. Mag. Ser. 6, Vol. 43. Pl. XVII.

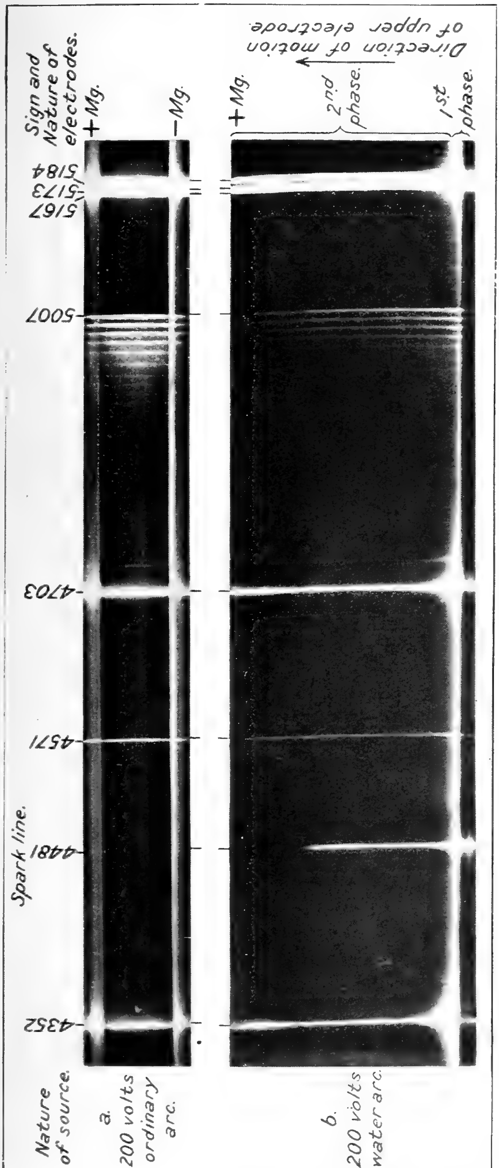


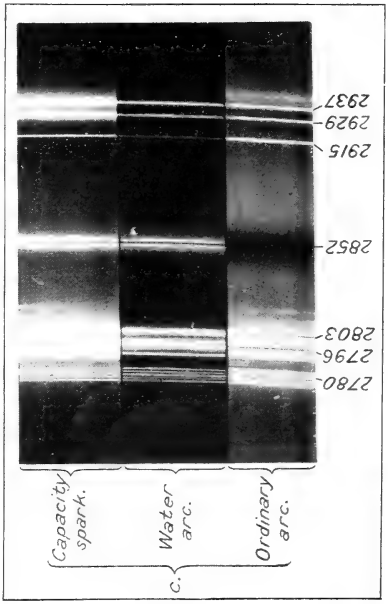
Arc Spectra of Magnesium (80 volts).



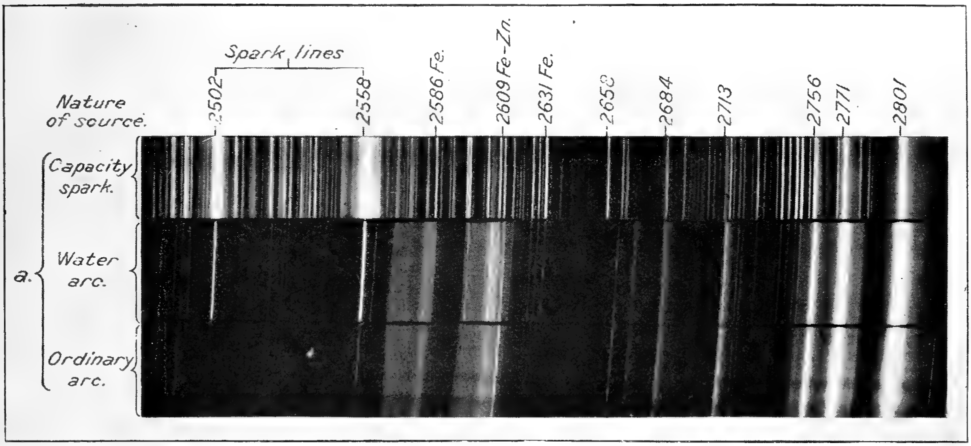
Arc Spectra of Magnesium (80 volts).

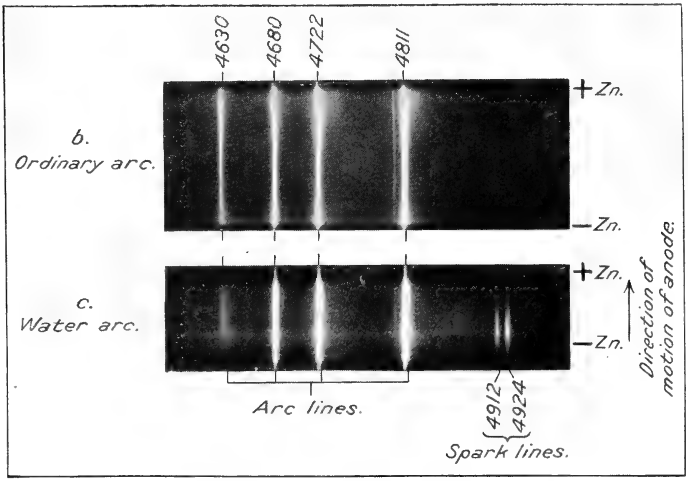
Arc and Spark Spectra of Magnesium.



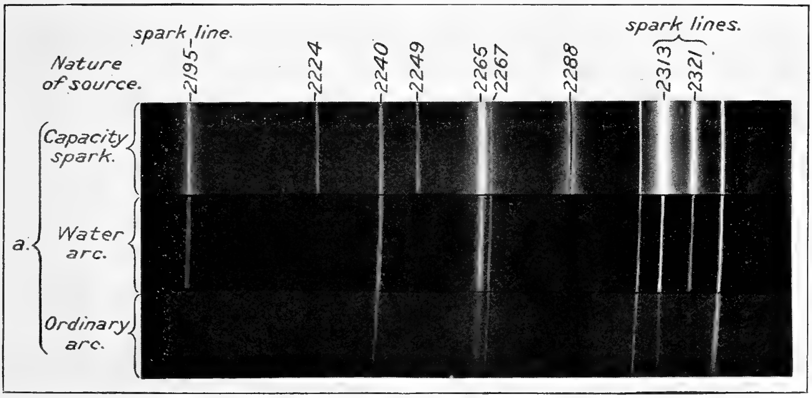


Arc and Spark Spectra of Zinc.





Arc and Spark Spectra of Cadmium.



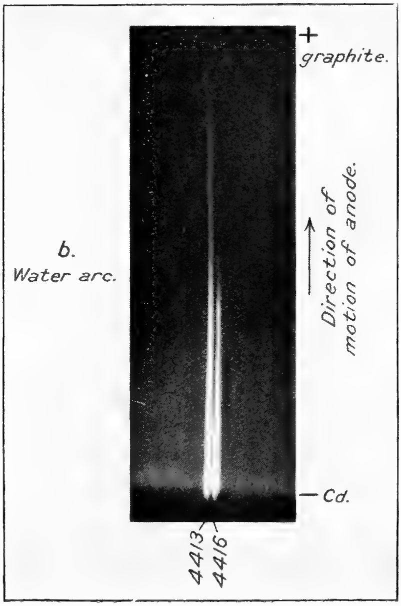
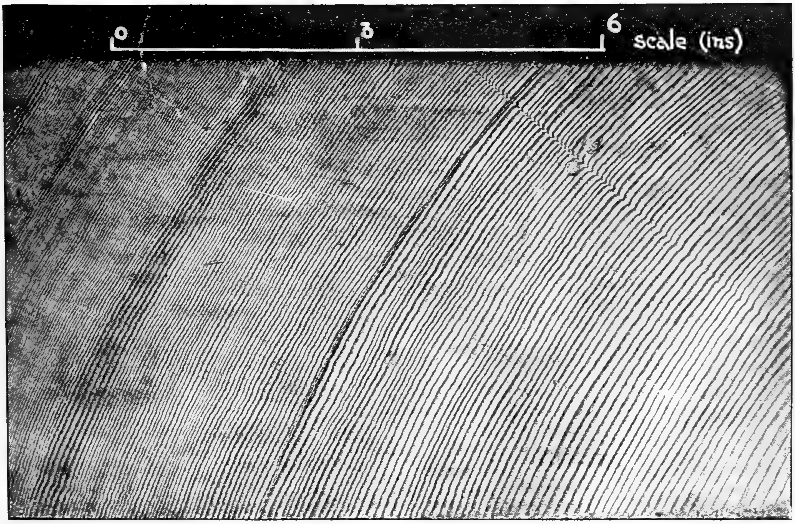


FIG. 1.



THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SIXTH SERIES.]

JUNE 1922.

CX. *The Hydrogen Molecule.* III.

By ALBERT C. CREHORE *.

IN the preceding paper † (II.) the case of two hydrogen atoms of the kind described ‡ in the first paper (I.) was treated in the special position where the two atoms are so aligned as to have a common axis, and the forces acting along this common axis alone were computed. A stable equilibrium in this direction was found when the distance between the atoms is $1{\cdot}18 \times 10^{-8}$ cm. Since this problem is typical of that with other forms of more complicated atoms, it seems important to investigate the character of the whole field around the central atom as affecting a second atom. The method followed in the previous paper has been applied here to cover the general position in space, always keeping the axes of revolution of the two atoms of hydrogen parallel, but no longer coincident or coaxial.

The only two forces that have any existence with this form of model are the electrostatic force together with the force due to the revolution of the positive and negative charges (electrons) upon their axes. The latter was completely developed in the first paper cited, equation (57), and may be called the gravitational attraction. It has been shown that no terms of higher order than the inverse square can be

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* Communicated by the Author.

† Phil. Mag. May 1922, p. 886.

‡ Phil. Mag. October 1921, p. 569.

effective in this latter force, and hence we possess the complete solution. The rigid solution for the electrostatic force between two oblate spheroids of charge in general positions is unknown, hence an approximation has been made to it, as explained in the second paper, by substituting for the negative electron a ring and a point, the solutions for which are known. The charge on the point situated at the centre is E_1, and that on the ring E_2, their sum being equal to the electron's charge, e. The ratio of the charge E_2 to e is defined as ρ, which evidently must be less than unity. This ratio is obviously determined by the eccentricity of the oblate spheroid, and it was shown to be equal to the square of this eccentricity in the previous paper. Taking the eccentricity $\epsilon = \cdot 945$ as determined in the first paper, the value of $1/\rho$ is, therefore, about 1·12.

The process followed has been indicated in detail in the second paper, and it is not practicable to give here more than a bare statement of the results obtained. These are all, however, derived in the manner described by the use of the inverse square law between infinitesimal elements of charge according to the principles of electrodynamics. A starting point may now be said to be the electrostatic force upon one electron due to a second, and, in the nomenclature employed before, this is given below as resolved into x- and z-components. The y-component has the same form as that of x, provided the direction cosine X outside the brace is exchanged for Y. The symbol $U^2 = X^2 + Y^2$ has been employed for brevity, and this may be converted into a function of Z only, since $X^2 + Y^2 = 1 - Z^2$.

$$\underset{\substack{\text{electron}\\\text{on}\\\text{electron.}}}{F_x} = \frac{e^2}{k} X \{ -r^{-2} + \rho a^2 f_{x,4}(U) r^{-4} + \rho a^4 f_{x,6}(U) r^{-6} + \rho a^6 f_{x,8}(U) r^{-8} + \rho a^8 f_{x,10}(U) r^{-10} + \rho^2 a^4 f_{x,12}(U) r^{-6} + \rho^2 a^6 f_{x,14}(U) r^{-8} + \rho^2 a^8 f_{x,16}(U) r^{-10} \ldots \}. \quad (1)$$

The z-force has the same form, but in place of the x-functions of U must be substituted z-functions, namely, instead of $f_{x,4}(U)$ write $f_{z,4}(U)$ and so on: also the direction cosine Z takes the place of X outside the brace. These functions have the following values:—

$$f_{x,4}(U) = 6 - \frac{15}{2} U^2, \quad (2)$$

$$f_{x,6}(U) = -\frac{45}{4} + \frac{315}{8} U^2 - \frac{945}{32} U^4, \quad (3)$$

$$f_{x,8}(\mathrm{U})=\frac{35}{2}-\frac{945}{8}\mathrm{U}^2+\frac{3465}{16}\mathrm{U}^4-\frac{15015}{128}\mathrm{U}^6, \quad . \quad . \quad . \quad . \tag{4}$$

$$f_{x,10}(\mathrm{U})=-\frac{1575}{64}+\frac{17325}{64}\mathrm{U}^2-\frac{225{,}225}{256}\mathrm{U}^4$$

$$+\frac{1{,}126{,}125}{1024}\mathrm{U}^6-\frac{3{,}828{,}825}{8192}\mathrm{U}^8, \quad . \quad . \quad . \quad . \tag{5}$$

$$f_{x,12}(\mathrm{U})=-\frac{45}{2}+\frac{315}{4}\mathrm{U}^2-\frac{945}{16}\mathrm{U}^4, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{6}$$

$$f_{x,14}(\mathrm{U})=\frac{315}{2}-\frac{8505}{8}\mathrm{U}^2+\frac{31185}{16}\mathrm{U}^4-\frac{135{,}135}{128}\mathrm{U}^6, \quad . \tag{7}$$

$$f_{x,16}(\mathrm{U})=-\frac{26775}{32}+\frac{294{,}525}{32}\mathrm{U}^2-\frac{10{,}495{,}485}{256}\mathrm{U}^4$$

$$+\frac{19{,}144{,}125}{512}\mathrm{U}^6-\frac{65{,}090{,}025}{4096}\mathrm{U}^8, \quad . \quad . \quad . \quad . \tag{8}$$

$$f_{z,4}(\mathrm{U})=3-\frac{15}{2}\mathrm{U}^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{9}$$

$$f_{z,6}(\mathrm{U})=-\frac{15}{4}+\frac{105}{4}\mathrm{U}^2-\frac{945}{32}\mathrm{U}^4, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{10}$$

$$f_{z,8}(\mathrm{U})=\frac{35}{8}-\frac{945}{16}\mathrm{U}^2+\frac{10395}{64}\mathrm{U}^4-\frac{15015}{128}\mathrm{U}^6, \quad . \quad . \tag{11}$$

$$f_{z,10}(\mathrm{U})=-\frac{315}{64}+\frac{3465}{32}\mathrm{U}^2-\frac{135{,}135}{256}\mathrm{U}^4+\frac{225{,}225}{256}\mathrm{U}^6$$

$$-\frac{3{,}828{,}825}{8192}\mathrm{U}^8, \quad . \quad . \tag{12}$$

$$f_{z,12}(\mathrm{U})=-\frac{15}{2}+\frac{105}{2}\mathrm{U}^2-\frac{945}{16}\mathrm{U}^4, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \tag{13}$$

$$f_{z,14}(\mathrm{U})=\frac{315}{8}-\frac{8505}{16}\mathrm{U}^2+\frac{93555}{64}\mathrm{U}^4-\frac{135{,}135}{128}\mathrm{U}^6, \quad . \tag{14}$$

$$f_{z,16}(\mathrm{U})=-\frac{5355}{32}+\frac{58905}{16}\mathrm{U}^2-\frac{7{,}432{,}435}{256}\mathrm{U}^4$$

$$+\frac{3{,}828{,}825}{128}\mathrm{U}^6-\frac{65{,}090{,}025}{4096}\mathrm{U}^8. \quad . \quad . \quad . \quad . \tag{15}$$

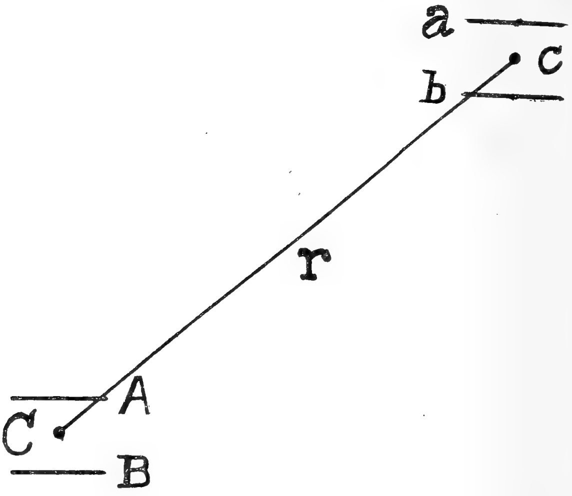
The next fundamental expression is the electrostatic force of the negative electron upon a point positive charge, *ne*, where n is a whole number. This is

$$\underset{\substack{\text{electron} \\ \text{on}+ne.}}{\mathrm{F}_x} = \frac{ne^2}{k}\mathrm{X}\{r^{-2}+\rho a^2 f_{x,18}(\mathrm{U})r^{-4}+\rho a^4 f_{x,20}(\mathrm{U})r^{-6}$$
$$+\rho a^6 f_{x,22}(\mathrm{U})r^{-8}+\rho a^8 f_{x,24}(\mathrm{U})r^{-10}\ldots\}, \quad . \quad (16)$$

with a similar expression for the z-component, having Z instead of X outside the brace, and z-functions within. These functions are

$f_{x,18}(\mathrm{U}) = -\frac{1}{2}f_{x,4}(\mathrm{U}) = -\frac{1}{2}$ of (2) above.
$f_{x,20}(\mathrm{U}) = -\frac{1}{2}f_{x,6}(\mathrm{U}) = -\frac{1}{2}$,, (3) ,,
$f_{x,22}(\mathrm{U}) = -\frac{1}{2}f_{x,8}(\mathrm{U}) = -\frac{1}{2}$,, (4) ,,
$f_{x,24}(\mathrm{U}) = -\frac{1}{2}f_{x,10}(\mathrm{U}) = -\frac{1}{2}$,, (5) ,,
$f_{z,18}(\mathrm{U}) = -\frac{1}{2}f_{z,4}(\mathrm{U}) = -\frac{1}{2}$,, (9) ,,
$f_{z,20}(\mathrm{U}) = -\frac{1}{2}f_{z,6}(\mathrm{U}) = -\frac{1}{2}$,, (10) ,,
$f_{z,22}(\mathrm{U}) = -\frac{1}{2}f_{z,8}(\mathrm{U}) = -\frac{1}{2}$,, (11) ,,
$f_{z,24}(\mathrm{U}) = -\frac{1}{2}f_{z,10}(\mathrm{U}) = -\frac{1}{2}$,, (12) ,,

Fig. 1.



Sectional view of two hydrogen atoms with parallel axes, ABC and *abc*. The electrons are represented as straight lines, since the ring and point approximation projects into a straight line.

The diagram, fig. 1, may represent the sectional view of the two hydrogen atoms now under consideration. ABC is the first atom, and *abc* the second. The distance, r, may be chosen as the distance between the centres of the positive charges C and *c*. The displacement of the centre of the electron A from the centre of C is the sum of the two minor axes of these spheroids, but since the minor axis of the positive charge C is very small in comparison the whole displacement is practically equal to the minor axis of the negative electron, or numerically, $1{\cdot}065 \times 10^{-13}$ cm.

The forces according to the above equation must then be written down for each pair of charges, one from each atom, with due regard to their actual distances, since the small displacement, b, is not negligible. This fact makes the process quite laborious, and we must content ourselves with giving the final result only, namely the whole force of the second atom upon the first. So far as the electrostatic part of the force is concerned the coefficients of the r^{-2} and r^{-4} terms of the series are zero, and only even terms appear thereafter. The gravitational equation (57) of the first paper above mentioned contributes, however, something to the r^{-2} term, and in the following result the term thus obtained is included. The force of the second atom upon the first may be written

$$\underset{\substack{\text{H-atom}\\ \text{on}\\ \text{H-atom.}}}{\mathrm{F}_x} \doteq \frac{2e^2}{k}\mathrm{X}\Big\{ \tfrac{1}{2} f_{x,26}(\mathrm{Z})\beta_2{}^4 r^{-2} + \frac{15}{2}\left(b^2 - \frac{1}{2}\rho a^2\right)^2 f_{x,28}(\mathrm{Z}) r^{-6} + \frac{105}{4}\left(b^2 - \frac{1}{2}\rho a^2\right)\left[(b^2 - 3\rho a^2)b^2 + \frac{3}{8}\rho a^4\right] f_{x,30}(\mathrm{Z}) r^{-8} + \frac{63}{8}\left[-\frac{9}{4}b^8 + \frac{31}{2}\rho a^2 b^6 - \frac{105}{16}\rho a^4 b^4 + \frac{5}{16}\rho a^6 b^2 - 15\rho^2 a^4 b^4 + \frac{45}{8}\rho^2 a^6 b^2 - \frac{85}{256}\rho^2 a^8\right] f_{x,32}(\mathrm{Z}) r^{-10} \dots \Big\}. \quad (17)$$

A similar expression answers for the z-component when X is changed to Z before the brace, and z-functions are substituted for x-functions, as for example, $f_{z,28}(\mathrm{Z})$ instead of $f_{x,28}(\mathrm{Z})$. These functions follow.

$f_{x,26}(\mathrm{Z}) = 1 + 3\mathrm{Z}^2$, ... (18)

$f_{x,28}(\mathrm{Z}) = -3(1 - 14\mathrm{Z}^2 + 21\mathrm{Z}^4)$, ... (19)

$f_{x,30}(\mathrm{Z}) = 5 - 135\mathrm{Z}^2 + 495\mathrm{Z}^4 - 429\mathrm{Z}^6$, ... (20)

$f_{x,32}(\mathrm{Z}) = 5(7 - 308\mathrm{Z}^2 + 2002\mathrm{Z}^4 - 4004\mathrm{Z}^6 + 2431\mathrm{Z}^8)$, . (21)

$f_{z,26}(\mathrm{Z}) = -1 + 3\mathrm{Z}^2$, ... (22)

$f_{z,28}(\mathrm{Z}) = -15 + 70\mathrm{Z}^2 - 63\mathrm{Z}^4$, ... (23)

$f_{z,30}(\mathrm{Z}) = 35 - 315\mathrm{Z}^2 + 693\mathrm{Z}^4 - 429\mathrm{Z}^6$, ... (24)

$f_{z,32}(\mathrm{Z}) = 315 - 4620\mathrm{Z}^2 + 18018\mathrm{Z}^4 - 25740\mathrm{Z}^6 + 12155\mathrm{Z}^8$. (25)

In the preceding paper the coefficient of the r^{-6} term containing the factor, say P, namely

$$P=b^2-\tfrac{1}{2}\rho a^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (26)$$

was taken as zero, and this supposition was shown to be quite in harmony with the previously determined shape of the electron. This expression equated to zero requires that the eccentricity of the oblate spheroid of the electron shall exceed about ·82, for, if it is less than this, the equivalent ring of radius a, that is employed in part to approximate to the electron, is shown to be greater than the equatorial radius of the electron, which is absurd. An inspection shows that the eccentricity must probably be greater than about ·9, and must fall between this figure and unity in order that the above factor shall vanish. And, because the eccentricity was determined to be ·945 by another method and at an earlier date, it seemed justifiable to assume it to be exactly zero and examine the result. Let us now again assume, first, that (26) is zero because of the shape of the electron and examine the result.

Since this quantity is a factor of both the coefficients of the r^{-6} and r^{-8} terms in (17), but not of the r^{-10} term, (17) becomes simplified as follows

$$\underset{\substack{\text{H-atom}\\ \text{on}\\ \text{H-atom.}}}{F_x} = \frac{2e^2}{k}X\Big\{\tfrac{1}{2}(1+3Z^2)\beta_2{}^4r^{-2} + \frac{63}{8}\Big(-\frac{125}{4}+\frac{75}{4\rho}-\frac{45}{16\rho^2}\Big)f_{x,32}(Z)\,b^8r^{-10}\ldots\Big\}. \qquad (27)$$

The z-force is similar, having Z for X before the brace and $f_{z,32}$ (Z) for $f_{x,32}$ (Z) substituted within it. Using the numerical values given above, namely

$$1/\rho=1{\cdot}12,$$
$$\beta_2{}^4=\cdot6053\times10^{-36} \text{ (see (82) first paper),}$$
$$b=1{\cdot}065\times10^{-13}\text{ cm. (see (79}a\text{) first paper),} \qquad (28)$$

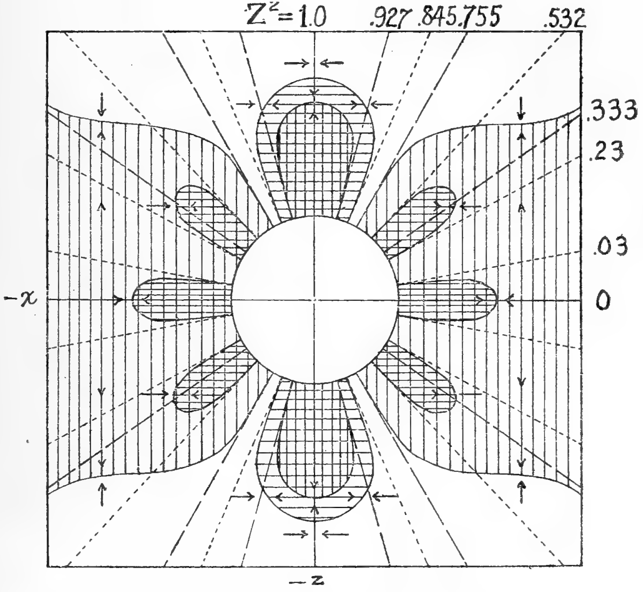
(27) becomes

$$\underset{\substack{\text{H-atom}\\ \text{on}\\ \text{H-atom.}}}{F_x} = \frac{2e^2}{k}X\{\tfrac{1}{2}(1+3Z^2)\cdot6053\times10^{-36}r^{-2} - 542{\cdot}5(7-308Z^2+2002Z^4-4004Z^6+2431Z^8)b^8r^{-10}\}, \quad . \quad . \quad . \qquad (29)$$

$$\underset{\text{ditto}}{F_z} = \frac{2e^2}{k}Z\{\tfrac{1}{2}(-1+3Z^2)\cdot6053\times10^{-36}r^{-2}-108{\cdot}5(315-4620Z^2+18018Z^4-25740Z^6+12155Z^8)b^8r^{-10}\}. \qquad (30)$$

The chart, fig. 2, is obtained by equating to zero the functions of Z and r within the braces of these equations. The caption under the figure is sufficient to render further description unnecessary. There is a point on the rotation axis (z) at a distance $1{\cdot}18 \times 10^{-8}$ cm. corresponding to the result at the conclusion of the second paper showing stable

Fig. 2.



The scale is indicated by the central circle with a diameter of 10^{-8} cm. The first H-atom is supposed to have its centre at the centre of this circle, and the second H-atom may be located anywhere with its axis parallel to the first, the z-axis. There are two sets of curves, the one where the x-component of the total force between the atoms is zero, and the other where the z-component is zero. These are indicated respectively by the horizontal and vertical hatching, which terminates on these two sets of curves. In the region of the horizontal hatching the x-force on the second atom due to the first is in a direction away from the axis of z, and in all other regions towards this axis. Similarly, in the region of the vertical hatching the z-force is directed away from the axis of x.

The chart is plotted from equations (29), (30), the gravitational term being balanced by the electrostatic r^{-10} term, the coefficients of the r^{-6} and r^{-8} terms being zero. There is no position of stable equilibrium here, since the x- and z-curves nowhere intersect. The angles where the tangents to the x-curves fall (the dotted lines) are given by the values of Z^2 in the margin. The tangents to the z-curves are shown by the dash-lines.

equilibrium in the direction of the axis, but there is no stability in a direction perpendicular to the z-axis at this distance. Before there is stability on this axis the distance must be greater than about $1{\cdot}32 \times 10^{-8}$ cm., where the x-curve crosses it. Indeed there is no point on the chart where the x and z curves intersect, and it is requisite that they should intersect for complete equilibrium, since the whole force must be zero; and there must also exist a restoring force for small displacements.

The hypothesis made above that P (26) is exactly zero is not, however, necessary, and it is quite unlikely on the theory of probability. All that has been shown is that it is probably small. This small value is entirely unknown unfortunately, so that the best that can be done is to assume different values for it large enough to have some effect upon the curves and see how the chart is thus modified. The chart of fig. 3 is the result obtained by taking

$$P = 3{\cdot}78 \times 10^{-35}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

The value is given to three figures simply because this is the particular value that happened to be used in making the chart. It lies between b^2 and b^3, not far from $b^{2{\cdot}65}$, and is such as to make the r^{-6} and r^{-8} terms of the series compare in magnitude with the other two terms at these distances, the r^{-2} and r^{-10} terms. To obtain a single point on one of the curves shown now requires the solution by approximation of a fifth degree equation, a much more tedious process than that required to chart fig. 2.

The result shows that there is now a definite position of stable equilibrium for the two atoms at the point where the x- and z-curves intersect, at an angle of latitude whose sine square is ·41 and latitude $\lambda = 39° \, 49'$. The distance between two atoms in the stable position is $\cdot 81 \times 10^{-8}$ cm.

A very great change has thus taken place in the result, changing fig. 2 into fig. 3 merely by using a value of P so small that it does not appreciably affect the approximation that

$$2\, b^2 = \rho a^2.$$

Although no other complete chart has been computed corresponding to another value of P than that used for fig. 3, it has been proved that when this value of P is doubled, nevertheless the angle of latitude at which the stable equilibrium occurs is not perceptibly changed, but the distance r is reduced from $\cdot 81 \times 10^{-8}$ to $\cdot 57 \times 10^{-8}$ cm.

The conclusion of this investigation seems to be that, in order to obtain a correct value of P with a high degree of accuracy, the distance between the two hydrogen atoms in the molecule must be sought from some other source. When the problem can be managed using some crystal, like the diamond say, where these distances are well known, this will afford a good value for the small residuum, P, and fix the property of the electron with considerable approximation.

Fig. 3.

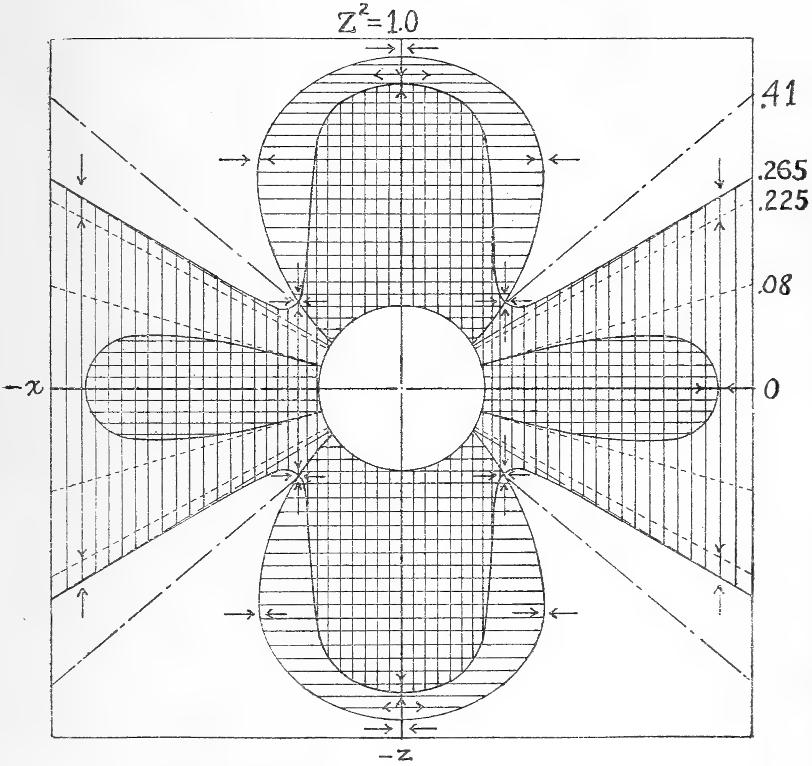


Fig. 2 changes into this figure when the value of P (26) is that given in (31). The coefficients of the r^{-6} and r^{-8} terms are now small but do not vanish. The curves are plotted from equation (17), the scale being the same as that of fig. 2. There is now a stable equilibrium position where the x- and z-curves of zero force intersect at an angle of 39° 49′ ($Z^2=\cdot41$), and at distance $r=\cdot81\times10^{-8}$ cm. The equilibrium distance for the z-force on the axis has increased from $1\cdot18\times10^{-8}$ cm. in fig. 2 to $1\cdot83\times10^{-8}$ cm. here.

In the case of gases it is believed that not much more is known about the distances between atoms in molecules than a rough approximation to their order of magnitude.

Perhaps as good an estimate as any of the distance between the two atoms in the hydrogen molecule has been made by E. C. Kemble *, who, however, assumes a dumbbell form of molecule, which by hypothesis has a different amount of freedom from the molecule above described. The above molecule is free to rotate around a circle of latitude at 39° 49′, but is not free to change this latitude without encountering a restoring force. Kemble makes use of the kinetic theory of gases combined with the quantum theory and arrives at a moment of inertia for the dumbbell, $2{\cdot}0 \times 10^{-41}$ gm. cm.^{2}, from which value it appears that the distance between the two atoms is about $\cdot 5 \times 10^{-8}$ cm. A slightly larger value of P than double that used for fig. 3 will give the equilibrium distance that is estimated from Kemble's result, but it seems desirable to revise his estimate in order to adapt it to this form of atomic model.

In concluding this part of the subject attention is directed to the fact that, except for numerical coefficients which are not very large, the values of the successive terms of the series for the electrostatic force are as b^4r^{-6}, b^6r^{-8}, b^8r^{-10}, etc., thus making the ratio of any term to the next following a constant, $b^{-2}r^2$ at a given distance, r. If r is of the order of 10^{-8} cm., since b is of the order 10^{-13} cm., the ratio is of the order $10^{26-16} = 10^{10}$, and the terms, therefore, decrease at a very rapid rate. Were it not for the fact that there exists a peculiar reason connected with the shape of the electron that makes the numerical coefficients of the r^{-6} and r^{-8} terms simultaneously very small, it would be quite unnecessary to consider the use of the r^{-10} term at all. This same peculiarity does not apply to the coefficients of the r^{-10}, r^{-12}, and subsequent terms, and as a consequence they follow the general rule above cited. Hence the r^{-12} and all following terms are quite negligible. The following Table I. gives the approximate values of the terms within the brace of (17) near the position of stable equilibrium for the two cases where P has the value used in making fig. 3 and for double this value. For the larger of the two values of P it is seen from this Table that the gravitational or r^{-2} term is becoming negligibly small in comparison with the other three terms. That is to say, the use of the electrostatic force alone is quite sufficient to cause a stable position to exist in the region of $\cdot 5 \times 10^{-8}$ cm. so far as the translational forces between the two atoms are concerned. The internal moment of the force which tends to keep the two atom's axes parallel

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* Phys. Rev. Feb. 1918, p. 156.

does, however, depend upon the rotation of charges upon their own axes, the β-terms.

TABLE I.

	r.	$r^{-2}\times 10^{20}$. term.	$r^{-6}\times 10^{20}$. term.	$r^{-8}\times 10^{20}$. term.	$r^{-10}\times 10^{20}$. term.
$P=3\cdot78\times 10^{-35}$, $Z^2=\cdot4$.					
x-force...	$\cdot79\times 10^{-8}$	1·067	16·41	− 7·677	− 9·595
z-force...	$\cdot81\times 10^{-8}$	0·922	11·075	17·39	29·26
$P=2\times 3\cdot78\times 10^{-35}$, $Z^2=\cdot4$.					
x-force...	$\cdot56\times 10^{-8}$	2·124	501	−233·1	−289·9
z-force...	$\cdot57\times 10^{-8}$	0-186	365	578·6	−983

This is rather a startling proposition, for it is well-known that no system of point charges alone without motion postulated can be so arranged as to produce a stable configuration for small displacements.

The Energy of Dissociation.

In the example of the two hydrogen atoms the forces have been given for the action of the second atom upon the first only, the individual parts not being expressed. The force, however, of the second atom upon the positive charge of the first is equal and opposite to the sum of the forces upon the two electrons at the position of equilibrium. These forces are each very great compared with their difference, which represents the whole force upon the atom. This may be proved by an examination of the equations above given, from which it will appear that the coefficient of the r^{-6} term is not small.

The effect of these forces is to increase the pressure between the positive charge, or nucleus, and one electron, and at the same time decrease the pressure between the nucleus and the other electron. The result must be to deform the shape of the four electrons very slightly, flattening one pair and increasing the minor axis of the other pair in the molecule.

The area of an oblate spheroid in terms of its eccentricity and semi-axes a_0 and b may be written

$$S_0=2\pi a_0^2+\frac{\pi b^2}{\epsilon}\log\frac{1+\epsilon}{1-\epsilon}. \quad . \quad . \quad . \quad . \qquad (32)$$

The area of a sphere of radius r having the same volume may be written

$$S=4\pi r^2, \qquad \text{where } a_0^2 b=r^3. \quad . \quad . \quad . \quad (33)$$

Dividing (32) by (33) the ratio of these areas is obtained as a function of the eccentricity alone,

$$\frac{S_0}{S}=\tfrac{1}{2}(1-\epsilon^2)^{-\frac{1}{3}}+\frac{1}{4\epsilon}(1-\epsilon^2)^{\frac{2}{3}}\log\frac{1+\epsilon}{1-\epsilon}. \quad . \quad . \quad (34)$$

Again, it may be shown that if the spheroid always maintains a volume equal to this sphere of radius r while its axes a_0 and b are changing, then

$$\frac{d\epsilon}{db}=-\frac{3}{2}\frac{b^2}{r^3\epsilon}. \quad . \quad . \quad . \quad . \quad . \quad (35)$$

Now differentiating (34) with respect to ϵ and multiplying the result by (35), we find the rate of change of the area of the spheroid with respect to the minor axis

$$\frac{dS_0}{db}=\frac{dS_0}{d\epsilon}\cdot\frac{d\epsilon}{db}=S\left\{-\frac{r}{2b^2}-\frac{3b}{4r^2\epsilon}+\left(\frac{b}{2r^2\epsilon}+\frac{3b^4}{8r^5\epsilon^3}\right)\log\frac{1+\epsilon}{1-\epsilon}\right\}. \quad . \quad . \quad . \quad (36)$$

Restoring the value of S (33) and using ΔS_0 for dS_0 and Δb for db, and multiplying the change in area of the spheroid by the surface tension T, (see (73) first paper), namely

$$T=\frac{3}{16}\frac{e^2}{\pi r^3 k}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

we thus find the energy required to change the shape of the spheroid by the small amount Δb as follows :

$$\Delta E=(\Delta S_0 \,.\, T)=\frac{e^2}{k}\Delta b\left\{-\frac{3}{8b^2}-\frac{9b}{16r^3\epsilon^2}\right.$$
$$\left.+\left(\frac{3b^2}{8r^3\epsilon}+\frac{9b^4}{32r^6\epsilon^3}\right)\log\frac{1+\epsilon}{1-\epsilon}\right\}. \quad . \quad (38)$$

Using numerical values

$$\left.\begin{aligned} r&=2{\cdot}244\times10^{-13}\text{ cm.}\\ b&=1{\cdot}065\times10^{-13}\text{ cm.}\\ \epsilon&=0{\cdot}945,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (39)$$

we find

$$\Delta E=\frac{e^2}{k}\Delta b(-0{\cdot}236\times10^{26}). \quad . \quad . \quad . \quad (40)$$

Two of the electrons of the molecule are contracted (or flattened) say by the amount Δb_1 while the other two are expanded by a slightly different amount, say Δb_2. Hence the change in the internal energy of the whole molecule from the state of free atoms may be written

$$\Delta E = 2(-0{\cdot}236 \times 10^{26}) \frac{e^2}{k} (\Delta b_1 - \Delta b_2). \quad . \quad . \quad (41)$$

The expansion of the minor axis Δb_2 may be assumed to be greater than the contraction Δb_1, so that one must supply energy to the molecule to restore it again into two separate atoms.

This is conceived to be the place where energy must be supplied to separate the two hydrogen atoms of the molecule, and the energy on this view is not only interatomic but also interelectronic. Using the experimental value of the energy of dissociation per H molecule as $5{\cdot}8 \times 10^{-12}$ erg as the value of ΔE in (41), it appears that

$$\Delta b_2 - \Delta b_1 = 5{\cdot}4 \times 10^{-19} \text{ cm.} \quad . \quad . \quad . \quad . \quad (42)$$

That is to say, the difference in the change of the minor axes of the two electrons in the one atom is very small indeed in order to correspond with what may be regarded as a rather large energy change. This is because the total energy content of the electron, mc^2, is $8{\cdot}08 \times 10^{-7}$ erg, and far exceeds the order of magnitude of the energies concerned in chemical transformations, of order 10^{-12} erg. Since the actual radius, b, of the electron is of an order a million times larger than (42) it seems most probable that the change in the shape of one electron (Δb) is of an order less than say the ten thousand part of the original radius.

Any change in the shape of the electron involves a corresponding change in its mass, but this change is so small that the change in mass must escape experimental detection, and this is true for the additional reason that the mass of the electron is already an almost negligible part of the atom itself. But this minute change is, however, entirely sufficient to manifest itself through the energy liberated or absorbed.

The small change in shape of the electron caused by the forces above mentioned when the atoms unite into one molecule, and which act in the proper sense to effect such a change, may account entirely for the observed energy of dissociation in all chemical combinations. This example using hydrogen as an illustration points to the seat of all such energies of combination well known to the chemist. Considering the character of the atoms described in the first part of the preceding paper, it is not difficult to understand that this energy may have a positive sign in some cases and a negative sign in other cases. Assuming that these views represent the truth of the matter, it is not difficult to see why such results as fill Thomsen's extensive work on Thermochemistry have never been successfully connected as yet with any sound theory. At the same time it revives a hope that this vast store of experimental evidence may soon be correlated with theory.

The important conclusion has been reached in this paper that the chief result in obtaining stable equilibrium for the two atoms of the molecule is independent of the special form of any electrodynamical theory, as for example the Saha or the Lorentz theory, since it depends chiefly upon the electrostatic force. All theories agree in making the electrostatic force between infinitesimal elements of charge follow the inverse square law.

Cleveland, Ohio.
Nov. 1, 1921.

CXI. *A Determination of the Number of α-Particles per Second emitted by Thorium C of known γ-Ray Activity.* *By* Allen G. Shenstone, *M.A.*, *and* Professor Herman Schlundt *.

RECENT experiments in the Cavendish Laboratory by Sir Ernest Rutherford and others have involved the use of the long-range α-particles from thorium C. The activity of the large thorium C sources used in those experiments was measured, as is customary, by means of a γ-ray electroscope. It has therefore become necessary to make an accurate determination of the number of α-particles emitted per second by thorium C of known γ-ray activity. Since that number is known for radium C, a direct comparison by count and by activity of radium C and thorium C will fix the number of α-particles per second emitted per mg. of thorium C. We have jointly carried out the experimental determinations.

Thorium C and its products produce, in the course of disintegration, α-rays of ranges 8·6 cm. and 5·0 cm. in air, in the proportion of 65 to 35. At the same time they produce hard γ-radiation. Radium C similarly emits hard γ-radiation

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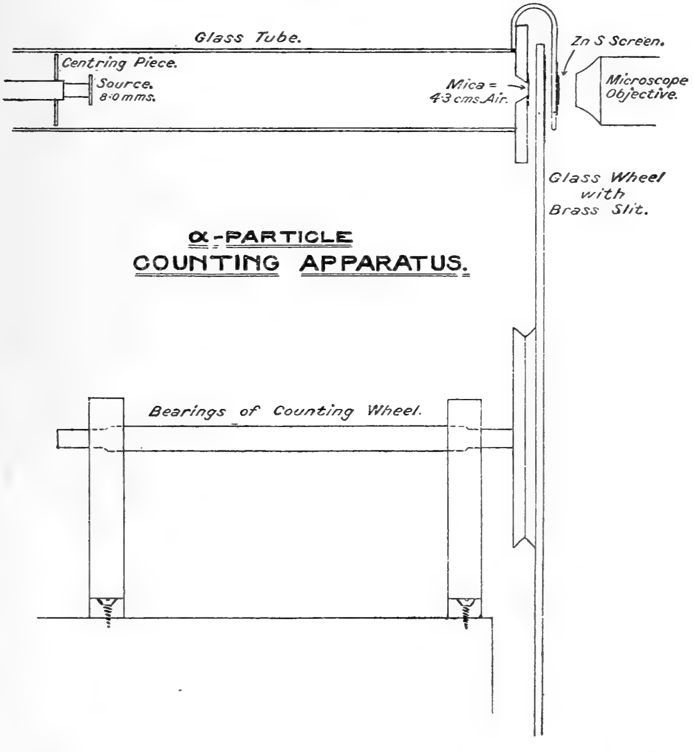
* Communicated by Prof. Sir E. Rutherford, F.R.S.

and α-particles of range 6·96 cm. and 3·8 cm., the latter, however, appearing in negligible numbers. In this experiment the α-particles counted were those of 8·6 cm. and 6·96 cm. range.

The deposit of thorium C was obtained in the usual way by rotating a nickel disk for about half-an-hour in a solution of radio-thorium. To obtain radium C a quantity of emanation was allowed to decay overnight, compressed in a small glass tube. The active deposit on the walls of the tube was then dissolved in 10 per cent. hydrochloric acid, and the radium C obtained by stirring the solution for about three minutes with the nickel disk. The disk used was of 8 mm. diameter, and was carefully protected by sealing-wax on the back and edges while depositing the active material. Check experiments on the back of the source showed that an inappreciable number of α-particles was emitted from it.

Fig. 1.



The experimental arrangement for counting is shown in the accompanying diagram (fig. 1). The nickel source was held centrally in a glass tube which could be exhausted by means of an aspirator. The end of the tube facing the source was closed by a brass plate having a central bevelled hole of 3 mm. diameter. This hole was closed by a thin sheet of mica of stopping-power equivalent to 4·3 cm. of air. The zinc-sulphide counting-screen was mounted on a bracket 8 mm. from the end of the tube. The total stopping-power in the path of the α-particles was therefore $4{\cdot}3+{\cdot}8=5{\cdot}1$ cm. of air *, which is just sufficient to prevent the 5 cm. α-particles from thorium C from reaching the screen.

The efficiency of a zinc-sulphide screen varies considerably over its surface. To ensure permanence of experimental conditions, it was therefore necessary to be certain that the same portion of the screen was always used. This was accomplished by mounting the screen with its crystal face against a piece of thin brass having a hole of diameter slightly less than the field of the microscope. The microscope could then always be focussed on the identical portion of the screen. The microscope used gave very bright images of the scintillations. It was fitted with Messrs. Watson's "Holos" × 5 eyepiece and "Holos" objective of ·45 n.a. and 16 mm. focal length. The usual "pea" lamp was used to slightly illuminate the screen.

The "Wheel" Method of Counting.

To enable large counts to be made with ease, a method of counting devised by Sir Ernest Rutherford was adopted. The essential feature of this method is the use of a disk of about 20 cm. diameter mounted with its edge intercepting the beam of α-particles. The disk is provided near its edge with a slit of suitable width which was 1·6 mm. in our case. The disk must be mounted on good bearings and must be fitted with a driving device capable of rotating it at a very steady rate of from 50 to 200 revolutions per minute. When the disk is rotating, the particles can reach the screen only when the slit is passing through the beam of particles. Moreover, the number of α-particles which can pass per minute is not a function of the speed of the wheel, but merely of the ratio of the width of slit to the circumference of the disk. The method of counting and recording also differs from the ordinary method. The observer does not mentally add the number of scintillations over a minute, but calls out the number which appears at each revolution of the

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* To this should be added about 0·2 cm. for the air left in the tube between the source and the mica disk.

wheel. The recorder writes down this series of small numbers, and they are added by minutes later.

The power of the method lies in the fact that calling out a seen number is merely a reflex action, whereas addition requires mental effort. The best observer cannot count with certainty above 65 or 70 scintillations a minute by the ordinary method; but with this wheel method up to 160 a minute can be recorded. Practice is, of course, required before the actions involved become quite mechanical. For a beginner, the wheel should be run as low as 50 a minute for counts averaging about 75 a minute, or about 1·5 per revolution. Later, the observer should have no difficulty calling out the numbers at a rate of 80 a minute for counts averaging two a revolution.

Ability to judge rather than to count the number of scintillations in a group is essential. An experienced observer can judge accurately up to groups of 7, mainly, in our experience, by the geometrical figures formed by the scintillations. Beyond 7 it is not usually possible to be absolutely certain of the number, but one must hazard a guess. Such large numbers should appear, however, extremely infrequently if the speed of the wheel is properly adjusted. We found that it was quite unsafe to count when the scintillations were appearing at a rate of over 2·5 per group on the average. When counting the particles from a decaying source and the number drops below 60 per minute, we found it easier to run the wheel about 200 revolutions per minute and to add the numbers mentally.

It is of interest to see the operation of the law of probability in the following examples of sequences of numbers called out during this work. A certain number of zeros should appear, but they were not noted.

½ minute:—1 2 3 1 1 4 2 2 1 1 3 1 4 4 3 2 2 2 3 3 1 3 3 3 1 2 1 4 1 4 2 3 1 1 1.

1 minute:—2 4 2 2 2 2 3 3 3 2 2 2 1 1 5 2 1 1 3 3 2 2 3 5 3 4 4 3 2 1 2 2 3 1 1 1 3 1 1 3 2 1 2 1 1 1 1 1 3 4 2 2 5 4 1 3.

½ minute:—1 2 2 2 3 2 2 2 2 1 2 2 2 2 2 1 1 2 1 3 1 3 1 2 2 1 1 2.

γ-Ray Measurements.

Since the comparison of the α-ray activities of the radium C and thorium C was to be based on equal γ-ray activities, it was necessary to have accurate γ-ray measurements at the same time as the counts. A γ-ray electroscope was mounted, therefore, about 30 cm. from the active source when in its counting position. The activity and decay of the source could then be measured by taking groups of readings while the count was in progress. Thorium C should fall to half value in 60·5 minutes and radium C in 19·5 minutes. Actually we obtained decay curves giving periods of 60 to 61 minutes for thorium C and 19·5 to 20·2 for radium C.

To calculate the result of a day's count, we first plotted the logarithms of the γ-activities against the time. The best straight line was then drawn through these points, and the γ-activity calculated from it for each half minute during which counting was carried on.

The number of particles counted per half minute per arbitrary unit of γ-activity is then obtained by dividing the total number of α's counted by the sum of all the γ-activities calculated. For counts on both thorium C and radium C the ratio of the numbers of α-particles emitted per $\frac{1}{2}$ minute for equal γ-ray activities is then obviously

$$\frac{\Sigma\,\alpha\text{-particles}}{\Sigma\,\gamma\text{-activities}}\text{ for thorium C} \div \frac{\Sigma\,\alpha\text{-particles}}{\Sigma\,\gamma\text{-activities}}\text{ for radium C.}$$

Such a ratio is independent of the dimensions of the apparatus as long as those dimensions remain unchanged during all the counts. The work was divided, therefore, into groups, and necessary adjustments to the apparatus were made only between groups. It will be seen in the following table that the ratios $\frac{\alpha}{\gamma}$ vary very considerably between groups, but that the ratios $\frac{\alpha\text{ radium C}}{\alpha\text{ thorium C}}$ do not differ by more than the probable error.

	THORIUM C.			RADIUM C.			$\frac{\text{ThC}}{\text{RaC}}$.
Group.	Count.	Activities.	Ratio.	Count.	Activities.	Ratio.	Ratio.
I.	2700	2506	1·08	2953	1993	1·48	·73
II.	1019	780	1·306	913	545	1·68	·78
III.	3191	2722	1·17	3515	2285	1 54	·76
IV.	3105	2231	1·39	3803	2100	1·81	·77
V.	3250	2411	1·35	2316	1246	1·86	·73
	13265			13500			

Weighted mean $\frac{\alpha\text{ ThC}}{\alpha\text{ RaC}}=0·75$.

The final ratio of $\frac{\alpha \text{ thorium C}}{\alpha \text{ radium C}}$ for equal γ-activities was computed as the mean of the group ratios, each weighted by the root of the number of α-particles included in the group.

Probable Error in Mean Ratio.

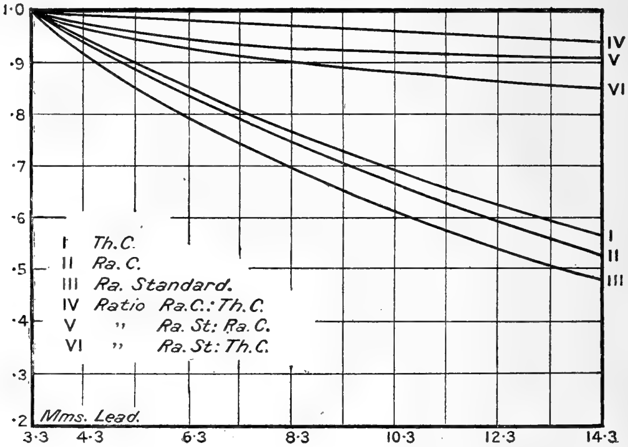
The probable error in the ratio ·75 arises from two factors. First, the error due to the finite number of particles counted. This is $100\left(\frac{1}{13265}+\frac{1}{13500}\right)^{\frac{1}{2}}=1{\cdot}22$ per cent. The other source of error is the electroscope and the plotting of the curves from the electroscope readings. The number of readings taken during a count was, on the average, 12. The probable error from a combination of 12 readings was computed by the formula $2/3\sqrt{\frac{\Sigma d^2}{\mathrm{N}(\mathrm{N}-1)}}$ from a large number of γ-ray measurements made on a radium standard. The highest value of the probable error obtained in this way was ·6 per cent. The error in drawing the logarithmic decay line through the plotted points is unfortunately impossible to calculate. It was certainly not greater than 0·5 per cent. Both these last errors enter twice, so that the probable error is given by $\{(1{\cdot}22)^2+2\times{\cdot}6^2+2\times{\cdot}5^2\}^{\frac{1}{2}}=1{\cdot}65$ per cent. The probable error calculated by the formula $2/3\sqrt{\frac{\Sigma d^2}{\mathrm{N}(\mathrm{N}-1)}}$, using the group values, is ·9 per cent., which is well within the error calculated above from the various factors separately.

It is of interest to note in this connexion the agreement between counts by the two observers. We differed by as much as 9 per cent. within groups, but our final ratios are only ·3 per cent. apart. The agreement is excellent evidence of the accuracy of the counting of both observers.

γ-Ray Absorption Measurements.

The γ-rays, in order to reach the interior of the electroscope used in this experiment, had to pass through a thickness of glass, lead, and aluminium having an absorbing power for the rays equivalent to 3·3 mm. of lead. In order to extend the application of the ratio of α emissions to comparisons through different thicknesses of lead, it was necessary to compare the absorptions in lead of the γ rays from thorium C and radium C. This was necessary because the coefficients of absorption given in the literature on the subject apply only to thicknesses of lead greater than 2 cm., and are far from the truth in the region below a centimetre. Curves I. and II. of fig. 2 are the result of γ-ray measurements on thorium C and radium C sources when increasing thicknesses of lead were placed between the source and the electroscope. It has been seen that the ratio of α-activities for equal γ-activities was computed as $\frac{\Sigma\alpha}{\Sigma\gamma}$ thorium C $\div$ $\frac{\Sigma\alpha}{\Sigma\gamma}$ radium C.

Fig. 2.

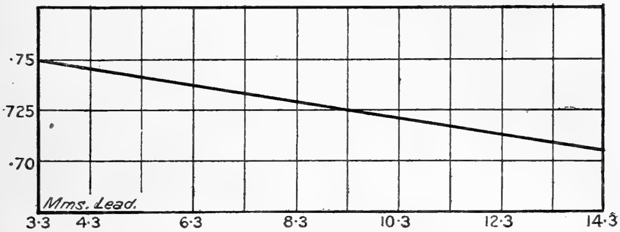


γ-Ray Absorption Curves.

In this expression the ratio $\frac{\Sigma\gamma \text{ radium C}}{\Sigma\gamma \text{ thorium C}}$ appears. Therefore if, from curves I. and II., we plot curve IV., the ratio of $\frac{\gamma \text{ radium C}}{\gamma \text{ thorium C}}$, that curve will give us the factors by which the ratio of α-emissions for equal γ-activities will be changed when comparisons are made of γ-activities between radium C and thorium C through greater thicknesses of lead. The curve obtained in this way, by multiplying the ordinates of curve IV. by ·75, is given in fig. 3.

The activity of a radioactive source is usually measured by comparing its γ-activity with that of a radium standard. The radiation of a radium standard consists in the main of two γ-radiations—a soft radiation from radium B and the hard radiation from radium C. The soft radiation is reduced practically to zero by passage through 1·5 cm. of lead. The absorption curve of the radium standard, therefore, should drop rapidly at first, and should finally attain a rate of fall identical with radium C. Consequently, if the ratio of the activities of a radium standard and radium C for different thicknesses of lead is plotted, it should show an initial fall, but a final constant value when all the radium B radiation has been absorbed. Curve III. fig. 2 is the absorption curve of the radium standard and curve V. is the curve of the ratio, radium standard/radium C, plotted from II. and III. The truth of the statements above is evident from this curve. The curve becomes flat at a value ·91. Consequently the ionization which was produced at 3·3 mm. of lead by the radium B in the standard, and which has been eliminated by 1·4 cm. of lead, must have represented 9 per cent. of the total ionization produced in the electroscope by the radiation from the standard.

Fig. 3.



Ratio of number of α-Particles ThC : RaC for equal γ-Activities.

The following table gives the γ-ray measurements from which the curves were plotted :—

Mm. of Lead.	Radium Standard.	Radium C.	Thorium C.
3·3	1·000	1·000	1·000
5·52	·836	·884	·890
7·62	·727	·777	·791
9·87	·631	·679	·705
11·95	·552	·597	·640
14·15	·484	·535	·565

The determination by Hess and Lawson* of the number of particles emitted by the amount of radium C which is in

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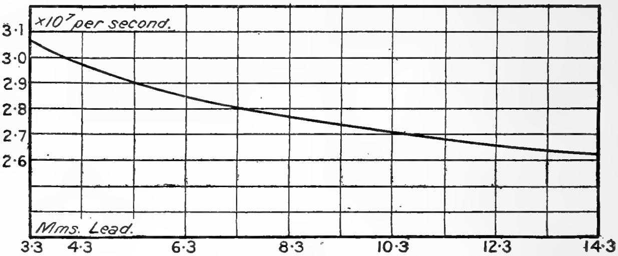
* Publication 105 of the Radium Institute at Vienna.

equilibrium with 1 mg. of radium is $3{\cdot}72\times10^7$ per second, with a probable error of ·54 per cent. But we have just seen that this amount of radium C gives only 91 per cent. of the total ionization produced by radium and its products. Therefore the rate of emission of α-particles by the amount of radium C which will give the same ionization as 1 mg. of radium when measured through 3·3 mm. of lead is $3{\cdot}72\times10^7\times\frac{100}{91}=4{\cdot}09\times10^7$ per sec. Consequently, thorium C of equal γ-activity emits at the rate of $4{\cdot}09\times10^7\times{\cdot}75=3{\cdot}07\times10^7$ per second. This number involves the error of 1·7 per cent. in the ratio ·75; the error of ·54 per cent. in the determination of $3{\cdot}72\times10^7$; the electroscope error of ·8 per cent. again entering twice in the absorption measurements; and the error due to the weighing of the lead sheets and variations in thickness of those sheets. This last error can only be estimated, but it should not be greater than 1·5 per cent. Combining all these factors gives a probable error of 2·5 per cent.

Fig. 4.



Number of 8·6 cm. α-Particles emitted by ThC of γ-Activity= 1 mg. Radium.

The amount of thorium C which will give the same amount of ionization in an electroscope as 1 mg. of radium and its products will vary with the thickness of lead through which the γ-ray measurements are made. In fig. 2, curves I. and III. are the absorption curves for thorium C and for a radium standard, and curve VI. is plotted from the ratios of the ordinates of curve III. to curve I. Starting with equal γ-activities of thorium C and radium at 3·3 mm. of lead, this curve VI. evidently gives the amounts of thorium C which will give at greater thicknesses of lead γ-activities equal to the γ-activities of the radium with which it is being compared. But, at 3·3 mm. of lead, thorium C of γ-activity = 1 mg. of radium and its products emits $3{\cdot}07 \times 10^7$ α-particles per second. Consequently, when comparison is made through a greater thickness of lead, the rate of emission of α-particles by thorium C is obtained by multiplying the corresponding ordinate of curve VI. by $3{\cdot}07 \times 10^7$. The curve obtained in this way is given in fig. 4, from which may be read the number of particles of range 8·6 cm. emitted by thorium C of γ-activity = 1 mg. of radium and its products for comparison through any thickness of lead between 3·3 mm. and 14·3 mm.

Our thanks are due to Mr. G. A. R. Crowe for the preparation of the sources used; and to Sir Ernest Rutherford and Dr. J. Chadwick, whose valuable advice rapidly eliminated our initial inexperience.

Cavendish Laboratory,
Cambridge, 1921.

CXII. *Restricted Movements of Molecules at very low pressures: A Limit of Applicability of the Second Law of Thermodynamics.* By Arthur Fairbourne, *Lecturer in Chemistry, King's College, London* *.

It has long been realised and has often been stated (compare Maxwell, 1871, 'Theory of Heat,' p. 308) that if sufficiently minute apparatus could be constructed to restrict, selectively, the movements of certain individual gaseous molecules so as to direct, for example, those with high velocities into one particular portion of a system and those with low velocities into another portion, then there would result in consequence of this selection a continuous creation of potential of temperature between these two portions of the system; a continuous creation of potential which would render the kinetic energy of the molecules continuously available for the performance of external work. Purely hypothetical apparatus for the satisfactory theoretical consideration of this possibility has been described, and much discussed (compare Maxwell, *loc. cit.*; Johnstone, 1921, 'The Mechanism of Life,' p. 215; Jeans, 1921, 'The Dynamical Theory of Gases,' p. 183), since the

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* Communicated by the Author.

possibility of continuous creation of potential is denied by the second law of thermodynamics.

It must be agreed, however, that any such continuous experiments as this, whether actual or hypothetical, fall definitely beyond the jurisdiction of the second law of thermodynamics, since they depend entirely upon the deliberate selection of particular molecules with specially desired velocities, while the second law considers and deals only with the average effects of large numbers of molecules of every variety of haphazard movement, acting together merely under the play of chance ; and the conclusion stated by this law is consequently entirely subject to the condition that no such deliberate selections of molecules with particular movements shall be made.

No record of any experimental verification of the effects of such selective restriction of certain molecular movements as are involved in these considerations has ever been put forward, nor has any means for performing such ever been suggested, and experimental verification has come in consequence to be regarded as unlikely, or, perhaps, impossible.

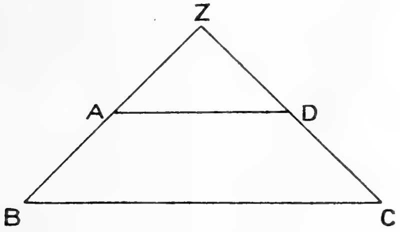
Although it may be impossible to construct an apparatus capable of selecting molecules travelling with certain desired *speeds*, yet it can be shown that it is not impossible to construct an apparatus capable of selectively affecting molecules travelling in certain desired *directions*, provided that portions of the apparatus to be used for this purpose are made smaller than the free paths of many of the molecules of the gas employed ; and, since the mean free path of certain common gaseous molecules at the easily realizable pressure of 1×10^{-2} mm. is calculated to be in the order of a centimetre in length, this requirement can be satisfactorily fulfilled without such difficulty as might have been anticipated.

Just as the deliberate segregation of molecules of particular speeds has been considered by Maxwell to cause the creation of potentials of temperature between the different portions of a system, so the continuous affecting or redirecting of molecules moving in certain desired directions only will cause corresponding differences (or potentials) of pressure on certain surfaces in the system.

The principle by which such selective directional interferences may be accomplished can be readily indicated by considering a long and narrow tube, ideally smooth and open at both ends, suspended in a gas whose mean free path is much greater than the length of the tube. Molecules enter freely at both ends, and most of those which happen to be moving in directions parallel or substantially parallel with the axis of the tube will pass through and out without any interference whatever to their motion, since the length is much less than the mean free path of the gas. Those, however, which enter at angles sharply inclined to the axis of the tube cross from side to side many times during their passage through the tube, and receive in this way many impacts from the walls. In fact, not only do they receive more impacts in unit time than do those which pass directly through the tube, but they also receive more impacts than do those outside the tube, since an extra restriction has been imposed * upon these molecules selectively.

With a suitable shape of vessel in place of the tube, it may be proved as follows that this extra restriction on the movements of the molecules can be applied selectively in such a manner that molecules which enter the vessel moving in haphazard directions will be diverted to leave it moving in one preponderating direction.

For the sake of simplicity, although the case is general, it will be assumed for the moment that the molecules are moving in two dimensions only, and it will also be assumed that the mean free path of the gas is so great in proportion to the size of the vessel that intermolecular collisions during the short journeys in the vessel are occurring with only a negligibly small fraction of the total number of molecules which pass through in any representative period of time.



Let ABCD be a two dimensional vessel, the shape of which corresponds to the cross sectional elevation of a truncated right angled cone. Let it be open at the top, AD, and bottom, BC, and, moreover, let BC be twice the length of AD.

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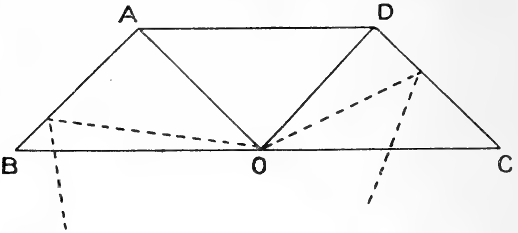
* Any gas in a hollow cube, the length of whose face is many times less than the mean free path of the gas, receives more impacts per molecule, in unit time, than does the same gas, at the same temperature and pressure, outside the cube, since, inside, no molecule can travel the calculated free path without receiving extra impacts from the walls.

Molecules enter through all points along both AD and BC, and at each of these points they enter in all possible directions. If the walls are assumed to be ideally smooth, or to behave as such with respect to impacts upon them *, then every molecule entering through AD, through any point, and in any direction, will necessarily pass out at BC, except in the very rare case where intermolecular collision occurs during its journey through the vessel. Of the molecules entering at BC, some pass out at AD, and others are returned through BC, two possible cases presenting themselves for consideration: (1) molecules entering through a point in BC under the opening AD; and (2) molecules entering through a point under either of the inclined sides, BA or CD.

Case 1: *Any point under the line AD.*

If the point be in the centre of BC (fig. 1), then all molecules entering in directions included by the angle AOD will pass out through AD, while all those entering in directions included by angles AOB and DOC will be returned through BC, owing to impacts on walls inclined at 45°. Since AOD is a right angle, and since molecules will enter equally in all directions throughout 180°, therefore half the total number of those entering through this point in any representative period of time will leave the vessel through the top, AD, the other half being returned through BC.

Fig. 1.



If the point be not in the centre (fig. 2), but still under AD, those molecules entering in directions included by angle AOD, which is less than a right angle, will escape through AD.

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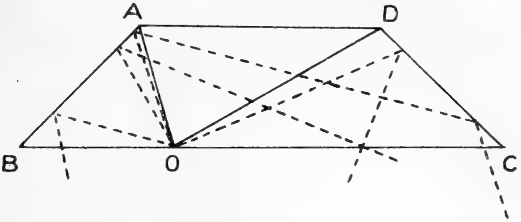
* The effects of irregular surfaces, and of adsorption on the surfaces, are considered later.

All those whose directions are included in angles DOC and AOB will either be returned through BC directly, or will be directed on to the opposite wall, and thence returned through BC. Thus more than half the total number of molecules entering through such a point as this will be returned through BC.

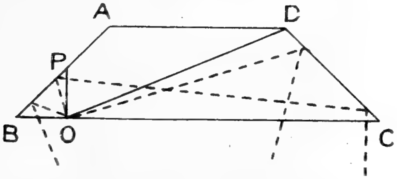
Fig. 2.



Case 2: Any point under AB or DC.

A perpendicular through O will cut AB (or DC similarly, if it be under DC). Let this point of intersection be called P. Since POB is itself a right angle, and angle DOC not small, therefore angle POD is considerably less than a right angle. Molecules entering in directions included in angle DOC are returned directly through BC. Those entering in directions included in angle POB are also returned through BC, either directly or after impact with DC. Only molecules entering in directions included in angle POD * succeed in reaching the top. Thus more than half of the total number of molecules entering through such a point as this will be returned through BC.

Fig. 3.



Thus of all possible points of entry through the line, BC,

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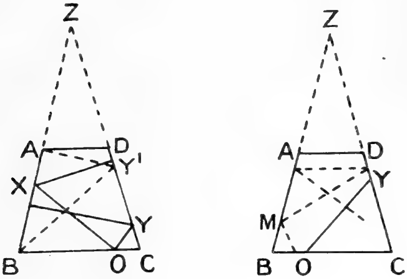
* And only some of these, namely those which enter in directions included in angle DOX, where X is the point on BA such that angle OXB is equal to angle DXA.

both those considered under case 1, and those considered under case 2, only that one point, which is midway between B and C will allow molecules entering equally in all possible directions to escape through AD to the extent of fifty per cent. All other points of entry on BC are placed so that the walls return through BC more than (and in most cases very considerably more than) half the total number of molecules which enter.

Let N molecules enter the vessel through AD in any representative or sufficiently long period of time, when, as has been shown, these all pass out through BC. Since BC= 2AD and two dimensions only are being considered, therefore 2N molecules enter the vessel through BC in this same period of time, but of these, whatever points they enter through, and whatever be their directions, more than half are returned through BC and less than half pass out through AD. Thus, while N molecules pass from AD to BC, less than half 2N, or less than N, pass from BC to AD: that is a downward flow has been created. This result (which is dependent upon the mean free path being so great in proportion to the size of the vessel that intermolecular collisions inside and in the immediate neighbourhood of the vessel are occurring with only a relatively small number of molecules) is due, as has already been explained, to a deliberate restriction or re-direction of movement applied selectively to molecules having certain velocity directions only (directions other than those included in angle BZC), and the effects of such restrictions have been shown to be theoretically independent of the second law of thermodynamics. This flow will produce a pressure potential on surfaces exposed to it, and external work can consequently be obtained at the expense of the kinetic energy of the gas enclosed in the system, precisely as in the case of the purely hypothetical experiment described by Maxwell.

The same effect may also be proved with equal simplicity for vessels with walls inclined to each other at smaller angles. For example, if BZC is an angle of 30°, from any point O on the base BC draw OX and OY, each at 45° to BC, cutting AB at X and DC at Y. OX and OY then meet AB and DC each at 60°, and are consequently reflected to strike the opposite side at 90°, whence it will be seen that all molecules entering at O, and travelling in directions included in angles XOB and YOC are returned through BC. This is true even in the extreme case where O almost coincides with B or C, since Y′BC and X′CB are themselves then each 45°. Angles YOC and XOB are together always equal to a right angle, wherever O may be situated, so that at least half of the total number of molecules entering through BC at all points, and in all directions equally, are returned through BC. Moreover, many molecules travelling at greater angles than 45° to BC are returned also (for example along OM, where angle

Fig. 4.



MOB=60° and angle YOC=45°), and therefore the resultant effect is as has already been proved for a vessel with an angle of 90°.

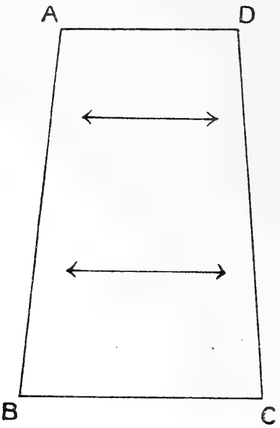
It can be shown further by similar reasoning that these results are true for vessels in which the height is greater than in those which have been dealt with, that is in which BC is greater than twice the length of AD.

In a consideration of three dimensional molecular movement, it will readily be seen that truncated pyramids and truncated cones must necessarily behave in the same manner, the additional velocity component producing its corresponding downward movement.

Only ideally smooth walls have so far been considered. Since polished surfaces are known to reflect even light, in the main, according to the usual laws of reflexion, although they are always very imperfectly smooth as seen under the microscope, it would consequently appear not unreasonable to suppose that this may be the general effect also where gaseous molecules are concerned, especially if the so-called molecular impacts be merely the bottoms of parabolic curves caused by the repulsion of the wall, but, in view of adsorption phenomena and other differences, such similarity of regular reflexion, even as an average effect, perhaps ought not to be premised, and it becomes desirable therefore to consider the effects which would be caused if the angles of reflexion were different from those of approach.

Actually the result must lie intermediate between the two extremes, (1) perfect reflexion, and (2) absolute independence of the angles of approach and departure. The first of these extremes has been considered. In the second it is desirable to consider a vessel whose height is greater than in those previously drawn, and whose angle, BZC, is small (fig. 5).

Fig. 5.



Let the vessel be imagined filled with a gas whose mean free path is relatively so large that intermolecular collisions during the short journeys in the vessel are occurring with only a negligibly small fraction of the total number of molecules which pass through in any representative period of time; and, at the first instant of consideration, let the molecules in the vessel be moving in all directions equally. If the walls were ideally smooth and the usual laws of reflexion were in operation, then any impact of a molecule, whatever its direction, with either wall (on the *inside* of the vessel) would necessarily increase the downward motion of that molecule, since all impulses caused by the smooth walls must be normal to their surfaces. Further, in this case, since the distance from wall to wall is less in the neighbourhood of AD than in that of BC, and since molecules pass from side to side without intermolecular interruption, therefore laterally moving molecules near the top of the vessel would receive more impacts from the walls in unit time than would those near the bottom *, thus suffering a greater total downward impulse than those in the lower layers; and as there is no balancing effect in their particular neighbourhood a downward flow must be produced, this conclusion being identical with that already obtained. The cause for such an effect has been explained in terms of an extra restriction selectively applied to molecules with particular movements, and would appear to be in strict accordance with the statements of Maxwell to which reference has been made. If, however, perfect reflexion were not in operation, and absolute independence of angles of approach and departure existed, then any point on the wall would discharge molecules haphazardly on either side of the normal to an equal extent, this being true, whatever theory of adsorption be adopted (compare Langmuir, J. Amer. Chem. Soc. 1916, xxxviii. p. 2221). Since the normal to either wall (inside the vessel) points downwards, and since this must be the mean direction of all discharge, and also of all approach so long as the molecules are moving equally in all directions, therefore hits upon the walls must still produce, in the main, downward impulses on the molecules concerned; and, for the reason given, these impulses are inflicted to a greater extent in the higher and narrower portions of the vessel than in the lower layers, whence the ultimate effect must be the same, qualitatively, as with perfect reflexion, although quantitatively it may not be so great. On the other hand it may be greater, for, if the theory of Langmuir (*loc. cit.*) on the repulsion of adsorbed particles be accepted, then these will probably be discharged from the sides mainly in directions substantially normal to the surface and will consequently leave the vessel through the base, thus giving an exalted effect above that to be expected in the case of ideally smooth walls and perfect reflexion.

A vane mounted with sufficiently minute friction inside or below one of the vessels described, while the vessel itself be suspended in a gas at a suitably low pressure, should therefore be capable in all cases of realizing experimentally the

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* Compare note p. 1049, which shows that although the pressure may be the same inside and outside the walls of a vessel, yet more impacts per molecule can occur inside than outside the vessel in the same period of time. So, in a vessel with converging walls, more impacts per molecule may occur in one portion of the vessel than in another. Assuming the concentration to be the same throughout the vessel, and the molecules to be moving equally in all directions, then the more constricted any portion of the vessel may be, the more frequently will molecules in that portion collide with the walls.

theoretical conceptions put forward by Maxwell, and should consequently yield mechanical work at the expense of the kinetic energy of the molecules ; that is of the temperature of the gas as a whole, a result which could not be obtained in any experiment coming within the application of the second law of thermodynamics.

General experience would indicate, however, that caution is desirable, in accepting this conclusion.

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CXIII. *Observations on the Construction and Use of the Steele-Grant Microbalance.* *By* E. J. Hartung *.

THE Steele-Grant microbalance has recently been applied by the writer to the study of the action of light on the halides of silver. During the course of the work some observations have been made on the construction and manipulation of the balance and on possibly unsuspected sources of error. It is hoped that these are of sufficient interest to be given here, as they have not always been emphasised, even in such an excellent article on microbalances as that of F. Emich (*Handb. d. biochem. Arbeitsmethoden*, ix. p. 55, 1919).

The microbalance was described by its inventors in 1909 (Proc. Roy. Soc. A. lxxxii. p. 580, 1909). It is made entirely from vitreous silica and consists of a rigid beam oscillating on a single central knife-edge in the more sensitive forms, or on a pair of edges for greater stability in the less sensitive forms. To one end of the beam a counterpoise of constant weight is fused, to the other a suspended system is attached by a fine silica thread. This suspended system consists of a light silica grid carrying the object to be weighed, as well as certain silica weights and a bulb containing a known quantity of air sealed in it. Equilibrium is attained, at first roughly by selection of the proper weights, and then accurately by adjusting the pressure in the balance case. The constant load is then made up of the object to be weighed, the weights and the apparent weight of the air-bulb, which varies with the density of the medium in which it is immersed.

For the investigation mentioned above, a balance of high relative sensitiveness was required. Pettersson (Proc. Phys. Soc. Lond. xxxii. p. 209, 1920) has modified the Steele-Grant

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* Communicated by the Author.

instrument by introducing a bifilar suspension in place of the knife-edge, and in this way he has succeeded in detecting differences in weight of only 0·25 μ ($1\mu = 10^{-6}$ mg.) in a load of 250 mg. This gives the almost incredible sensitiveness of 1 part in 10^9, though presumably the actual working sensitiveness would not be so great. The Pettersson type of balance was therefore eminently suitable, but it was not used because the balance cases available were designed for the original knife-edge type of Steele and Grant. The most sensitive balance of the inventors was able to detect changes in weight of about 4μ, but the load is not stated and apparently it was not great. Their type-B balance with double knife-edges would measure differences of 100μ in a load of 100 mg., giving thus a relative sensitiveness of 1 part in 10^6. This appeared to be sufficient for the proposed work, and an instrument of this type was therefore constructed. Its constants were as follows :—

Period 33 seconds. Maximum load 43 mg. Minimum indication 20μ. Accurate weighings could be made to within 40μ, giving a relative working sensitiveness of 1 part in 10^6.

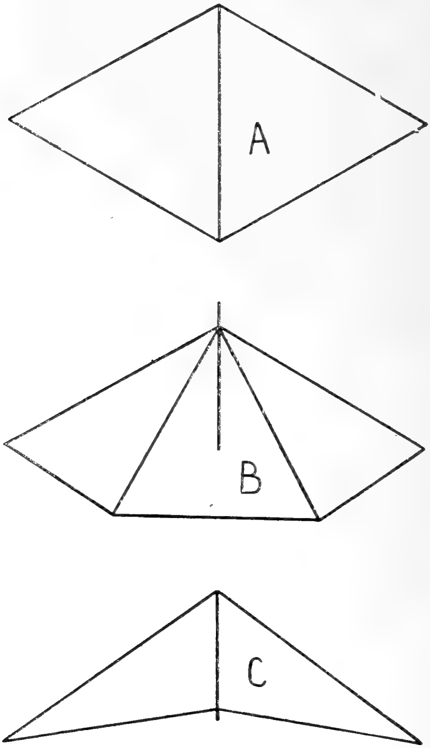
Experiments were also performed with some other types of balance, differing in structural details, and the general conclusions reached through a comparative study are given in the following paragraphs.

The Beam.

The correct design of the beam is of the first importance, as it must combine rigidity with lightness and therefore with economy of material. The best form is undoubtedly the rhombus with vertical diagonal (fig. 1, A), as adopted finally by Pettersson, but it is not suited for knife-edges. The original design of Steele and Grant is exceedingly good, and it is not easy to see how to improve it. Gray and Ramsay (Proc. Roy. Soc. A. lxxxvi. p. 270, 1912) evidently considered that it was not sufficiently strong, and in their classical work on the atomic weight of radium they employed a new type of beam (fig. 1, B). The radium balance which they constructed was a very trustworthy instrument, and the results they obtained leave nothing to be desired; the maximum load was 24 mg., which could be weighed to the nearest 14 μ, thus giving a relative sensitiveness of about 1 part in 2×10^6. However, from a theoretical point of view, it is not by any means clear what advantages the radium balance beam possesses over the simple double-triangle type of Steele and

Grant (fig. 1, C). It is inherently heavier for the same strength because the material is less economically distributed, and the absence of the vertical rod connecting the upper and lower portions probably increases the tendency to fail laterally under load. Further, the placing of the knife-edges at the end of a comparatively long pillar attached by only one complex joint to the rest of the structure is a device of problematical value. In order to test the limitations of the double-triangle beam, a balance of this type was constructed with a single knife-edge about 0·4 mm. long. The members from which the beam was made were carefully selected, and special pains were taken to fuse them together strictly in one plane. The instrument was adjusted so that its period of oscillation was about 90 seconds, and it was then capable of detecting a difference of 1μ in a load of 40 mg. This

Fig. 1.



corresponds to a relative sensitiveness of 1 part in 4×10^7; in use, however, the resting-point was found to vary slightly from day to day, so that trustworthy weighings could not be obtained beyond the nearest 4μ. This gave a relative working sensitiveness of 1 part in 10^7. One may therefore venture to state that the simple Steele-Grant type of beam leaves little to be desired as to trustworthiness and constancy of behaviour, and there is no reason to discard it in favour of other types. For comparatively heavy loads, the thickness of the members may be proportionately increased and the requisite sensitiveness attained by suitably raising the centre of gravity.

The Knife-edges.

Steele and Grant, in their original memoir, described the process by which the knife-edges had been made by them. They were ground in sets of three by means of a small rectangular metal holder into which silica rods had been cemented. By resting the ends of the rods and the long edge of the holder on a ground glass plate supplied with a little fine abrasive, alternate grinding on both sides resulted in chisel edges. The thickness of the holder was then increased by securing steel slips on either side, and the operation was finished on a very finely-ground glass plate with a little glycerine and water but without abrasive. This method requires only comparatively simple apparatus and is capable of giving very satisfactory results; it has been employed in the present work. The greatest difficulty is found in the finishing touches. The glass plate employed must be heavy and very steady, truly flat, and with so finely ground a surface that it is almost transparent when dry. It has been found advantageous to use a very light forward stroke with abundance of lubricant for the final polishing, and the edges must slide over the glass without the slightest harshness or hesitation. The progress of the work is watched with a microscope, the edges being carefully dried before examination; they may be taken to be good enough when the irregularities are barely visible with a good 5-mm. objective.

Pettersson criticizes rather adversely the knife-edge type of balance on the ground that dust collecting on the quartz bed-plate will interfere with the free movement of the edge and that it will gradually become blunted through use. These disadvantages do not attend the bifilar suspension which he adopts, and he makes out a strong case for the superiority of his method, in spite of the greater difficulties in construction and adjustment. However, the theoretical and practical simplicity of the knife-edge as a point of support is a strong recommendation in its favour, and, moreover, the results of the present work show that Pettersson's criticisms are largely unfounded for balances of minimum indication not less than 1μ. No trouble has been experienced from dust and, far from deteriorating, the edges seem actually to improve with careful use ; this is no doubt due to the gradual removal of the infinitesimal raw edge left after grinding.

It is necessary to arrange the arrestments of the balance so that the beam is merely arrested in its movement when not in use and the knife-edges are not lifted away from the plate. If the beam is lifted when the instrument is not in use, the resting-point will not remain steady, particularly in the more sensitive types. Steele and Grant mention this in their paper, but do not explain the reason ; probably it is due to irregular distortion of the knife-edge. Calculation shows that in the sensitive balance described above, the centre of gravity of the system is not more than ·001 mm. below the edge, while, in spite of the lightness of the beam and its accessories, the pressure on the edge is intense owing to its very small bearing surface. A slight distortion may therefore have serious influence on the equilibrium position of the beam, and it is probable that the wandering of zero after lifting the beam is due to slow alteration in this distortion, which only becomes permanent and constant when the knife-edge rests continuously on the plate.

The Fibre Suspension.

Steele and Grant found that a fine silica fibre suspension from one end of the beam was more satisfactory and much more easily managed than the knife-edge and plane suspension used on ordinary analytical balances. They drew the fibre directly from the beam by hand. An improved process is due to Mr. G. A. Ampt, of Melbourne University. He fuses a weighted hook to the beam by a small, very thin rod, and then passes a minute oxy-gas flame repeatedly and very rapidly across this rod. The result is a fine fibre which gradually extends and can be drawn to any desired thinness at any point. Gray and Ramsay (Proc. Roy. Soc. A. lxxxiv. p. 536, 1911) fused a long fibre direct to the beam, and obtained in this way a very free suspension for their niton balance. The desideratum of a good fibre is that it bends very sharply at one point so that it approximates to the ideal point and plane suspension. The bending, however sharp, must necessarily take place through a small arc, with the result that as the end of the beam rises it lengthens slightly, and as it falls it shortens slightly. This departure from the ideal suspension may show itself in three ways:—

(i.) The sensitiveness of the balance will depend to some extent on the positions at which weights, etc., are hung on the rack carried by the fibre.

(ii.) The actual resting-point of the balance will depend to some extent on these positions.

(iii.) The values obtained by calibrating the weights against the air-bulb will depend to some extent on the relative positions of weights and bulb on the rack.

All these points could be observed with the double knife-edge balance before described, which was tested for the purpose. The suspended system here consisted of a short fibre about 2 cm. in length which carried the air-bulb of volume 332·8 cubic mm. Hanging from the lower end of this was a fine rod about 10 cm. long, fashioned below into a rack and terminated by a small hook. The whole system was about 14 cm. long and is shown in fig. 2. Table I. shows the alteration in resting-point and in sensitiveness consequent on hanging a standard weight of 43 mg. in positions A, B, or C.

TABLE I.

Position of weight.	Sensitiveness in divisions per 100 μ.	Equilibrium case pressure.	Change in weight.
A....	5·0	542·1 mm.	100 μ
B....	3·8	541·9 ,,	50 μ
C....	3·5	541·8 ,,	

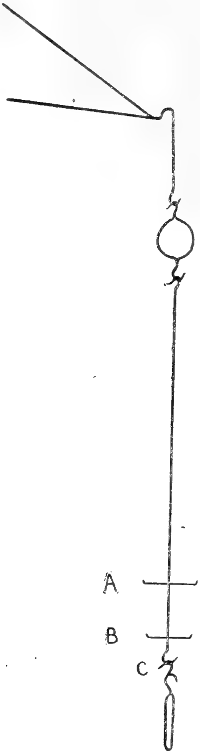
It will be observed that the sensitiveness increases with the height of the load. The resting-point has also altered, for a vertical change in position of the load of 2 cm., by 150μ in a load of 43 mg., *i.e.* by 1 part in 3×10^5. Though small, the alteration is appreciable, but it becomes negligible if the load is always hung at the same level.

Table II. shows the alteration in apparent value of three selected weights as calibrated against the air-bulb when two different fibres were employed. As these fibres differed somewhat from one another in length, the relative positions of air-bulb and weights in the suspended system were not the same in the two cases.

TABLE II.

Weight.	Value with fibre 1.	Value with fibre 2.	Percentage increase.
1....	0·2590 mg.	0·2596 mg.	0·23
2....	0·5910 „	0·5923 „	0·22
3....	1·0370 „	1·0395 „	0·24

Fig. 2.



The difference between the two sets of values is considerable, and neither would agree with the true values obtained when bulb and weights are hung at the same level. This last procedure is therefore to be recommended, although it is not really necessary unless absolute weighings are required.

The slight variation in the percentage alterations as given in the fourth column is doubtless due to an unfortunate accident during the two sets of weighings. The stand carrying the silica weights was overthrown, and the weights had to be cleaned from dust and fluff which adhered to them. Such cleaning operations, even if very carefully carried out, are always liable to leave slight residual changes in weight.

It is very likely that the variations shown in the tables could be materially diminished by the employment of thinner and longer fibres. The long and free fibre suspension used by Gray and Ramsay is probably much superior in these respects, but no tests have been made with it. Attention is merely directed to possible sources of error in the use of the balance. It should also be borne in mind that the risk of breaking the fibre during the ordinary manipulations connected with weighing is considerably increased with very thin fibres, and the delay consequent on the insertion of a new fibre and the readjustment of the whole balance may be very annoying. In this connexion it may be worth mentioning that a very neat device, due again to Mr. G. A. Ampt, renders such manipulations comparatively safe. All weights, counterpoises, and objects to be weighed are provided with two hooks, one above the other, as shown in fig. 2 They then hang on the balance or on their stands from the upper hook, and are carried from place to place on a slender silica rod from the lower hook. When it is desired to hang an object on the balance, the upper hook is allowed to engage with one of the arms of the rack, and the silica rod is slipped out of the lower hook without straining the fibre in the least. The operations are reversed when an object is removed from the balance. The adoption of this simple device will save much worry and trouble.

General Arrangement of Apparatus.

It is almost needless to remark that the precautions against dust, mechanical shocks, and temperature changes, emphasised by various workers, must be carefully followed if accurate results are required. In the present work the balances were mounted on rubber pads in a cellar with concrete floor which was almost free from vibration and maintained a fairly steady temperature. The cases were surrounded by metal boxes as advised by Gray and Ramsay, and the indicating light was only allowed to impinge on the mirror momentarily and after passage through at least 25 cm. of distilled water. The manometer was connected to the cases by means of long, narrow glass capillary tubes bent in the form of long loops ; this served the double purpose of protecting the instruments from shocks and from air-currents which would be engendered by rapid alterations of pressure in the case. The air which is allowed to enter must be dried by passage over suitable reagents, and subsequently filtered through tightly-packed cotton-wool. It is not advisable to introduce drying agents into the case itself. Gray and Ramsay noted that when air was allowed to enter rapidly, slight shifts in resting-point were observed, and they attribute this to the lodgment of dust particles on the balance ; the source of this dust was doubtless the solid barium oxide which they put into the case for drying purposes. Phosphoric anhydride is particularly liable to cause such trouble.

My thanks are due to Mr. J. A. Smith for much useful information on the design of balance beams.

Chemical Laboratories,
University of Melbourne ,
October 1921.

CXIV. *The Interaction between Radiation and Electrons.*

By C. F. Bickerdike *.

In a "Report on Radiation and the Quantum Theory" to the Physical Society (1914) Jeans examines the question of the equilibrium distribution of energy between electrons and the æther. In a paper in the 'Philosophical Magazine' June 1914 he points out that the substantial difficulty of reconciling the facts with dynamical theory arises not in connexion with the mere propagation of radiation in the æther conceived as a continuous medium, but solely in the interchange of energy between radiation and matter. He applies the equations appropriate to the motion of a charged particle acted upon by radiation, and deduces that the only final state of equilibrum would be one which is not to be reconciled with the facts observed experimentally. His inference is that "the departure from the classical mechanics is to be looked for in the fundamental equations of æther and electricity."

The writer ventures to suggest that possibly the classical conception of Faraday lines may afford a clue to the direction in which to seek for the solution of the difficulty.

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* Communicated by the Author.

The equations used by Jeans were originally derived with reference to the motion of a charged particle, the mass being that of the particle, the electrical inertia of the charge being negligible. In applying the equations to the electron, the material mass of the particle is dispensed with and the electrical inertia of the charge substituted.

If, instead of dealing only with mathematical equations, we picture the charge as consisting of radiating Faraday lines which extend indefinitely through the æther—and which presumably are states of the æther itself,—this picture at once suggests the question whether the radiation acts directly on the lines, the centre or body moving as a result of motion first imparted to the lines, or whether, on the other hand, the motive force is applied directly on the centre or body of the electron and the lines are dragged after it. In the theory of the effect of an acceleration applied to a charged body as causing emission of radiation, it is always conceived that the force is applied to the body and the lines of the charge dragged after it. When there is no material "body," it may still be the case that that is the mode of application of an acceleration to a negative electron when the force is the attraction of a positive, which is conceived as a tension along the length of some of the lines. It is rather to be expected, however, that when one negative electron acts on another, by radiation, the case will be substantially different, and the action may be directly on the lines of the receiving electron. The centre may then move in conformity with the motion already imparted to the lines, and it may be quite inadmissible to infer that acceleration of the centre so produced would result in the emission of radiation in the manner in which emission would result if the acceleration of the centre has been produced by a force acting directly on that centre.

It may be objected that the radiation, on first approaching the electron, must reach the centre at least before it has reached the lines which extend in the direction away from that in which the emitting electron lies.

In reply it may be pointed out that the first arrival of the front of a wave of radiation is a very brief moment. Actually, in all experimental work, we have to deal with a long train of radiation, and the question what exactly happens just at the moment of the arrival of the first wave is relatively unimportant. The receiving electron is very soon surrounded on all sides equally by æther affected by the radiation, and it is suggested that, for a free electron, the receipt of radiation is the converse of the emission. In the case of emission we conceive the centre as moving first, dragging on the ends of the lines and sending flexures outwards. Conversely, when radiation is absorbed, flexures travel inwards from the outer parts of the Faraday lines, and the centre moves in accordance ; but that motion does not itself produce an outward flexure *so long as it is unopposed.* At all events, the kind and degree of such action must be quite different from what it would be if the centre were itself first acted upon independently of any pre-existing motion of the lines.

When, however, the electron comes up against the inertia of a positive the situation is necessarily different. There may be either reflexion or transmission. *Prima facie* one would associate transmission with a state of things in which there is no scope for free motion at all, and complete reflexion with a state of things in which there are free electrons which have already absorbed radiation up to a critical point.

The general nature of the argument may be illustrated by a comparison with a vessel floating in water—notwithstanding the fact that such analogies are liable to be very misleading. A wave generated in the water moves the vessel up and down—*i. e.* the vessel receives accelerations. We should be very much in error, however, if we were to infer that these accelerations in turn produce waves in the water in the same degree and manner as if they were produced by some force acting directly on the vessel and plunging it up and down in water which was otherwise at rest.

It is a different situation again, however, if the vessel is tied by a string to a weight at the bottom of the water so that it is not free to move in conformity with the wave ; but whether that offers any useful analogy with the case of the bound electron is difficult to say. We have to recollect that the vessel is something existing independently of the water, and substantially not affecting the state of the water, whereas the electron really consists of lines which are presumably states of the æther and not something existing independently. We are not entitled to liken the lines to rods stretching out from the vessel into the water, but not forming part of the water. The analogy of a vessel in water has, however, the limited use of calling attention to the importance of distinguishing between the conditions under which an acceleration is produced as bearing on the effects to be inferred.

If the suggestion is tenable that the perfectly free electron will receive and absorb radiation up to some critical point without emission at all so long as its motion is unhampered, it seems clear that in general the shorter the wave-length of the radiation, the greater the possibility of its being so absorbed, because the length of free path necessary to fulfil the condition would be correspondingly small and would the more frequently occur. There would therefore be selective absorption of small wave-length vibrations, and the tendency for the energy all to be absorbed into smaller and smaller vibrations would be prevented.

The electron which constitutes part of the system of an atom also may be able to absorb similarly, since, within limits, it may be free to move in the direction perpendicular to the plane of its orbit. In that way it also may be a selective absorber of the smaller wave-lengths of radiation.

The writer is disposed to go further, however, in criticism of the argument that energy must, on Newtonian principles, fritter away into the minutest chaotic motions. It is submitted that the possibilities of thermo-dynamic analogy have not been exhausted, and that even if we forget the Faraday lines and treat the electron in the æther as analogous to a heavy particle in a kind of gas composed of far more minute particles than any ordinary material gas, the argument that the heavy particle must lose all its energy does not necessarily hold good when we proceed from the finite case to the infinite, or when we at least entirely alter the order of magnitude of our gas molecules.

Jeans* takes the formula for distribution of energy between N molecules of air at temperature T and n heavy spheres. "The total energy in the steady state will be $(\frac{5}{2}N+\frac{3}{2}n)RT$, and T will be determined from the condition that this quantity must be equal to the total energy of the original oscillations of the spheres. Since N, the number of molecules, will be enormously large compared with n, the number of spheres, it is clear that practically all the energy will be contributed by the term $\frac{5}{2}NRT$. By the time the steady state is reached the energy is almost entirely transferred from the spheres to the gas."

The principle is the same if the energy is dealt with in terms of sound-waves.

The question is, however, whether, if we are going to make N enormously greater than it would be in the case of any actual gas, there are not some considerations to be taken into account which can be neglected as unimportant so long as we are dealing with familiar gases.

Starting from the conception of a familiar gas, such as air or hydrogen, having N molecules in a given space, we must

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* Report, p. 5.

first have a conception of how the change is being made when we imagine N to be increased *ad infinitum.* If we simply add to the number of air-molecules, with the average kinetic energy per molecule unaltered (except so far as may be the result of abstracting energy from the heavy particle) we are packing our finite space with an infinity of mass and of energy. No one can conceive what this would mean—whether the gaseous molecules have any room to move at all, in fact.

Let us, first of all, therefore, conceive the air-molecules as diminished in mass just in proportion to the increase in their numbers. We can imagine each molecule—supposed originally as uniformly of mass m—to be divided into x parts, and x can be made as large as we like. The original mass and density of the gas are then unaltered, and its total energy is unaltered excepting for transference from the heavy particles *.

The accepted laws of distribution of energy are arrived at on the supposition that the actual time of any collision is so small in comparison with the time of free motion of each molecule that it can be neglected, and the heavy particle is conceived as colliding *successively* with individual molecules of the gas.

If the mean length of free path is l originally and the radius of the molecules is r, l is assumed to be so much larger than r that r is negligible†.

When we suppose each molecule to divide into x parts, l and r are diminished indefinitely, but remain of the same order of magnitude relatively to one another.

On this supposition it is possible that the time required

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* It is clear that on this hypothesis the formula of Jeans (Report, p. 6) for total energy in terms of energy of waves would not have the meaning which he attributes to it. λm is the limiting wave-length, which may be made as small as we like provided it is not comparable with the average distance between molecules. The total energy is $\frac{4\,\mathrm{RT}}{3\,\lambda m^3}$. Jeans says this gives infinite energy when λm is infinitely small. This can only be on the assumption that RT is not similarly reduced in magnitude and must imply that M is increased *ad infinitum* by mere addition of molecules with the same mass and energy as the original ones, *i. e.* packing the finite space with infinite mass and energy. Of course, if that could be conceived, the energy of the heavy particles would be small in comparison. If we multiply N, however, by the method proposed above, the total energy is unchanged and RT must be reduced as much as λ_m^3. This consideration alone, however, does not suffice to dispose of the argument that the energy of the heavy particles would all go into the gas.

† *Vide* Edgeworth, "On the Application of Probabilities to the Movement of Gas Molecules," Phil. Mag. Sept. 1920, pp. 249, 250 and footnote.

for the interchange of energy at collisions would diminish in the same ratio, and, if so, the principles applicable to the partition of energy would possibly be unaltered, provided that the velocities attributed to the heavy particles were not much smaller than the average velocity of the gas particles.

There is, however, an important new condition introduced. The probability laws governing the distribution of energy in gases are arrived at by conceiving encounters to take place between heavy and light particles *successively*. When we have multiplied the light particles *ad infinitum*, however, by the process of division above suggested, we have now to conceive that instead of the mass M having successive encounters, altering its velocity as stated, for instance, by Edgeworth, there would be *simultaneous* encounters on all sides. In a direction at right angles to the motion of M there would be no momentum given to M. When the velocity of M is comparable with the velocities of the light particles, however, there would be more particles in contact with M in front than in the rear, and M would lose momentum.

In working towards something supposed to be analogous to the æther, however, we may postulate very high velocities for the ultimate particles—velocities, say, of the order of magnitude of the velocity of light. In that case, a heavy particle moving in such a medium, with velocity of a lower order of magnitude, would have practically as many light particles, at any moment, in contact in front as in contact behind. The impacts would be transmitted through M, which would have its velocity unaltered. M, then, once in uniform motion, would move through such a gas as through a perfect fluid, without loss of energy—or only extremely slow loss.

It may be objected that electrons also have very high velocities, and that they are the "heavy particles" dealt with by Jeans. The introduction of high velocities involves, however, a further consideration which can be neglected in dealing with ordinary gases.

The length of the free path is made indefinitely small, although, if we keep to the idea of a limitation of the amount of mass (*i. e.* conceiving the masses to be diminished in proportion to the increase of numbers), there is still the possibility of motion of the individual particles. The time occupied by free motion may be so reduced, however, that it is no longer small compared with the time occupied by an encounter, and may be less than such time.

In that case, the heavy particle, being impinged upon by a light particle, the two would have parted company before other light particles had impinged upon the rear of the first one. The heavy particle would, in fact, be charged not successively by single light particles, but by battalions of them in column. Equilibrium would be reached when, on an average, the columns were of mass equal to that of the heavy particle. The equilibrium could occur even though the velocities of the heavy particles were of the same order of magnitude as that of the lighter particles.

Under those conditions the law of final partition of energy would be entirely different from that which would result merely by making N large in the formula for gases.

Whether this would give a credible picture of the æther which would conform with other facts, it is not the intention here to discuss.

It would seem to imply a medium which would not be quite like æther, a gas, or a liquid, or a rigid solid, but having some of the properties of each.

The only point insisted on here is that such a thing is conceivable, and, although the Newtonian laws are assumed, there would not be that frittering down of all energy into the smallest movements. One exception alone is all that is necessary to disprove the generality of the argument that the Newtonian laws must always lead to this conclusion about dissipation of energy.

Conceptions of the æther on these lines may have been thought of before. Novelty is not claimed, but the writer is not aware that the bearing of such a conception on the theory of partition of energy has been pointed out.

CXV. *On the Spectra of X-rays and the Theory of Atomic Structure.* *By* D. Coster[*].

[Plate XXIII.]

Part I.

Introduction.

§1. ACCORDING to Bohr's theory of spectra the frequencies of the lines in the X-ray spectrum of an element may be represented by the difference of two terms which correspond to the energies of the atom before and after the emission. Following Barkla's original notation for the different kinds of characteristic X-radiation, the various

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[*] Communicated by Prof. Sir E. Rutherford, F.R.S.

groups of energy-levels whose existence may be inferred from the X-ray spectrum are usually denoted as K, L, M, N... levels. As pointed out by Kossel, these levels may be assumed to be connected with the different groups of electrons in the atom, in such a way that the various energy terms correspond to the work required for the removal of an electron from one of these groups. The various groups of electrons of the atom are in consequence often termed the K-, L-, M-, N- ... shells. This interpretation of the levels affords an explanation of the laws governing the absorption in the X-ray region: it is well known that this absorption is not connected with the single lines in the spectrum but extends over spectral regions which are sharply limited by the so-called absorption edges, the frequencies of which correspond to the energies of the levels concerned. Corresponding to the different ways in which the removal of an electron from a shell may take place we obtain several levels for each shell.

As has been pointed out by Sommerfeld, part at any rate of this complexity in the groups of levels may be connected with the complexity of the ensemble of the stationary states of the hydrogen atom. According to Sommerfeld's theory of the fine structure of the hydrogen lines, the stationary states of an atom containing one electron are characterized by two quantum numbers. One of these numbers, which we shall term the total quantum number n, is the same as that occurring in Bohr's interpretation of the simple formula for the hydrogen spectrum. The other number is the so-called "azimuthal" quantum number, which determines the value of the angular momentum of the electron round the nucleus, and which we shall denote by k.

§ 2. In his recent publications* Bohr has developed a theory of atomic structure which contains certain essentially new features, and which seems to give a natural interpretation of the periodic system and at the same time to offer an explanation of the results of Kossel and Sommerfeld on the X-ray spectrum. According to Bohr's theory, the orbits of the electrons in the different groups of the atom are characterized by different total quantum numbers, this number being equal to 1 for the innermost group (K-shell), 2 for the next group (L-shell), and so on, every time increasing by one unit until the surface of the atom is reached. Within each group the electrons are again divided into sub-groups, corresponding to different types of orbits and characterized by different values of k. A survey of the gradual development

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* 'Nature,' March 1921 and October 1921. See also for a fuller account, *Zeitschrift f. Physik*, ix. p. 1 (1922).

of these groups and sub-groups with increasing atomic number is illustrated by the following table, which indicates the proposed constitution of the atoms of the inert gases.

Element.	Number of electrons in n_k orbits.																				
	1_1	2_1	2_2	3_1	3	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6
Helium 2 ...	2																				
Neon 10 ...	2	4	4																		
Argon 18 ...	2	4	4	4	4	–															
Krypton 36 ...	2	4	4	6	6	6	4	4	–	–											
Xenon 54 ...	2	4	4	6	6	6	6	6	6	–	4	4	–	–	–						
Niton 86 ...	2	4	4	6	6	6	8	8	8	8	6	6	6	–	–	4	4	–	–	–	–

§ 3. In previous papers * I have been able to show that nearly all the lines of the X-ray spectra of the heavier elements can be arranged in a simple scheme, involving the existence of one K-level, three L-levels, five M-levels, and seven N-levels †, and that in continuation of the work of Sommerfeld it is possible to characterize every level in a definite way by means of two quantum numbers n and k as defined above. Further, the appearance of the observed X-ray lines was found to be governed by two simple "rules of selection." According to the first rule only those combinations between two levels will appear, for which the quantum number k remains unaltered or changes by one unit. The second rule ‡ states that the levels may be divided

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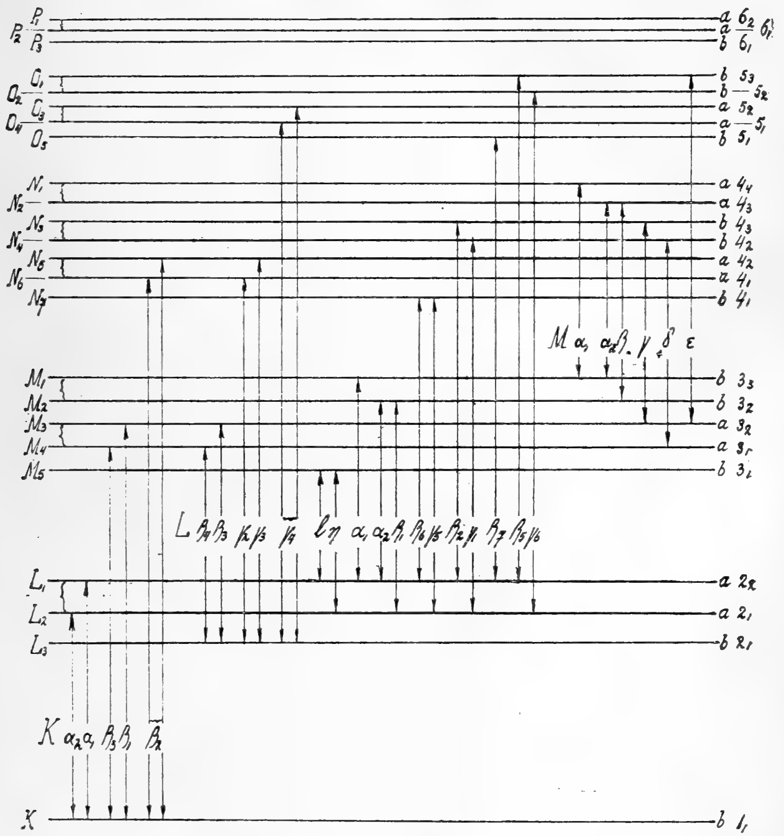
* *Zeitschrift f. Physik*, v. p. 139 (1921), denoted in the following by I., and vi. p. 185 (1921), (denoted by II). Compare also: A. Smekal, *Zeitschr. f. Phys.* v. p. 91 (1921), and v. p. 121 (1921); A. Dauvillier, *C. R.* clxxii. p. 1350 (1921), *C. R.* clxxiii. p. 35 (1921), *C. R.* clxxiii. p. 647 (1921); G. Wentzel, *Zeitschr. f. Phys.* vi. p. 84 (1921); A. Sommerfeld and G. Wentzel, *Zeitschr. f. Phys.* vii. p. 86 (1921).

† This also suggests that we must expect the existence of one K-, three L-, five M-, and seven N-absorption edges. These absorption edges have actually been found in the K- and L-series, by several authors for different elements, and recently I have been able to establish the existence of five absorption edges in the M-series for U and Th. (See Phys. Rev. II. xix. p. 20, 1922.)

‡ This rule of selection has been stated independently by Sommerfeld and Wentzel in another way. They introduce a third quantum-number, "Grundquantenzahl." This number is equal to or one unit larger than the azimuthal quantum number. The transitions are subject to the condition that this "Grundquantenzahl" must change by one unit. As we do not yet know the physical meaning of this "Grundquantenzahl," it seemed to me better to state this rule of selection in the same way as it was first suggested to me by Mr. H. A. Kramers.

into two types, *a*-levels and *b*-levels, in such a way that every observed line appears as a combination of one *a*- and one *b*-level, while combinations of two *a*- or two *b*-levels do not appear *. It will be seen, that in consequence of the latter rule we never observe lines, the frequencies of which are the exact sum or difference of the frequencies of two

Diagram I.—NITON.



other lines. An illustration of this classification of the X-ray spectra is given in diagram I. for niton, which is based

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* It should be mentioned that some very weak lines have been observed which represent a transition $b \rightarrow b$. They are the transition L_3–K observed only for W by Duane and Stenström and the lines $L\beta_9$ (transition M_1–L_3) and $L\beta_{10}$ (transition M_2–L_3) observed by several authors for various elements. (See *Zeitschr. f. Phys.* ii. p. 200, table 9.)

on measurements for elements of atomic number preceding or following that of niton (86)*.

Comparing this diagram with the above table representing the results of Bohr's theory, we see that it has been possible to characterize the levels by the same quantum-numbers as those which in the niton atom characterize the different groups and subgroups. We may now assume that the existence of the levels indicated in diagram I. is connected with the appearance of the various subgroups of electrons in the atom. Further, we may assume that in those cases where more than one level is characterized by the same quantum numbers, we witness different processes of removal of an electron from the same subgroup, the remaining electrons in the group arranging themselves afterwards in different ways.

§ 4. These conclusions obtain strong support from an inspection of the way in which the energy differences of the levels corresponding to the various values of n and k vary with the atomic number N of the element. The considerations in question rest upon a comparison with the theory of the stationary states of an atom consisting of a single electron revolving round a positive nucleus. In the first approximation, where the motion of the electron is calculated according to Newtonian mechanics, the energy necessary to remove the electron from one of these states to an infinite distance from the nucleus depends only on the total quantum number n. This energy is given by Bohr's formula,

$$W=N^2\frac{hcR}{n^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is the number of unit charges on the nucleus, h Planck's constant, c the velocity of light, and R a universal constant appearing in the theory of spectra and called the Rydberg constant. The theoretical value of the latter constant is given by the relation

$$R=\frac{2\pi^2e^4m}{h^3c}=109737, \text{ (number of wave-lengths per cm.)},$$

where e is the charge of the electron and m its mass for velocities small compared with the velocity of light.

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* As to the nomenclature of the lines, which often differs very much with different authors, I have in this paper in general used that proposed by Prof. Siegbahn. Still, for a theoretical discussion it may be advantageous to use sometimes another nomenclature analogous to that used for the visible region. According to this latter one, *e. g.*, the lines $K\alpha_2$ and $L\gamma_2$ may be called KL_2 and L_3N_5 respectively.

Taking into account the variation of mass with velocity required by the theory of relativity, the energy necessary for the removal of the electron from one of the stationary states is, to a first approximation, given by Sommerfeld's formula,

$$W=\frac{N^2hcR}{n^2}+\frac{N^4hcR\alpha}{n^4}\left(\frac{n}{k}-\frac{3}{4}\right), \quad . \quad . \quad . \quad (2)$$

where k is the azimuthal quantum number and α a numerical constant small compared with unity, the theoretical value of which is given by

$$\alpha=\left(\frac{2\pi e^2}{hc}\right)^2=5{\cdot}30\,.\,10^{-5}.$$

Formula (1) gives an interpretation of the general laws which had been revealed by Moseley's fundamental discoveries. According to these laws the energies of the observed levels are closely proportional to the square of the atomic number, the energies of the K-, L-, and M-levels being approximately represented by the formulæ

$$W_K=Rhc(N-a_K)^2,\ W_L=\frac{Rhc(N-a_L)^2}{4},\ W_M=\frac{Rhc(N-a_M)^2}{9}, \quad . \quad . \quad . \quad (3)$$

where a_K, a_L, and a_M are constants which are different for the different levels. The appearance of these constants in formula (3) is simply explained by taking into consideration the interaction of the electrons in the atom; the main effect of these is virtually to reduce the attractive influence of the nucleus on the electron whose removal corresponds to the level under consideration. The constant a is therefore often termed the "screening-constant" belonging to the level; and the quantity $(N-a)$ may be called the effective nucleus charge.

From formula (2) we obtain an explanation of the circumstance that certain pairs of energy-levels corresponding to the same value of n vary to a close approximation as the fourth power of the atomic number. Following the notation of Sommerfeld, such pairs of levels may be termed "relativity doublets," since the energy-difference between the two orbits is due to the differential effect of the relativity modification on orbits having the same value of n but different values of k. In the diagrams these pairs of levels are denoted by {.

As stated above, for levels having the same values of n and k we should expect that differences in the energy necessary to remove an electron from the atom would arise from different orientations of the orbits of the remaining electrons within the group concerned. In such levels it may be said that the remaining electrons can have different screening effects. This offers a simple explanation of a fact revealed by an inspection of the measurements, that the energy-differences between two such levels to a close approximation vary linearly with the atomic number. Such a pair of levels may therefore be termed "screening doublets" *.

In this connexion, however, it must be pointed out, that the numerical values of the screening constants for the different levels calculated from the relativity doublets do not agree with those calculated from the screening doublets †. This is just what we might expect from Bohr's theory of atomic structure. According to this theory the electrons of the outer shells come during their revolution round the nucleus wholly inside the orbits of the inner shells, so that they are moving in a varying field of force. Now it is easily seen, that the effect of the relativity change of mass on the orbit of the electron is mainly due to that part of the orbit which lies close to the nucleus, and where the velocity is very great. We thus understand that the screening constant for these electrons appearing in the relativity term of formula (2) has another value than that appearing in the main term which in first approximation gives the whole energy of the orbit.

§ 5. In general, corresponding to a given pair of values for n and k there exist two levels, of which one is of the type denoted in the above diagram as an a-level, the other a b-level. For the largest value of k corresponding to any given value of n there appears, however, only one level. I am indebted to Prof. Bohr for the remark that this circumstance may be brought in suggestive connexion with his theory of atomic structure, which rests upon a consideration of the way in which an atom may be formed by the successive binding of the electrons by the nucleus. In fact, in such a process the subgroups corresponding to the highest value of k will correspond to the electrons bound during the last stage of formation of the group, and, in contrast to the removal of an electron from subgroups corresponding to

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* Sommerfeld divides the doublets into "regular" and "irregular" doublets. As the screening doublets show no irregularity at all, these names seem not to be well chosen.

† Compare Sommerfeld and Wentzel, *Zeitschrift für Physik*, vii. p. 86 (1921).

smaller values of k, the removal of an electron from this subgroup may therefore be expected to represent a simple and well-defined reversal of a step in the process of formation of the group.

In this connexion it must be pointed out that the proposed explanation of the origin of these levels requires that the screening constants for a pair of levels corresponding to a relativity doublet should have approximately the same value. No simple explanation of this, however, is offered in the present state of the theory.

§ 6. Though there still remain some difficulties, we may say that the X-ray spectra are built up in a simple manner and that there exist many analogies between these spectra and the series spectra in the visible region. There are also, however, some striking differences. In the visible spectrum, transitions in which the azimuthal quantum number remains the same do not occur under ordinary conditions. In the X-ray spectrum, however, there are several lines for which k remains constant. A few of them are fairly intense lines (*e. g.*, in the case of the heavier elements $L\beta_4$ and $L\beta_3$ and also $L\gamma_2$ and $L\gamma_3$ are of about the same intensity). Recently I have found that there is another difference between the X-ray spectrum and the visible spectrum. In the latter there exist also transitions for which the total quantum number n does not change at all. To these belong for instance the first line of the principal series of the alkali metals. From this we might expect that the transition L_1–L_3 would give rise to a line in the X-ray spectrum which might easily be detected. An investigation with a tungsten anticathode showed, however, that this line does not exist at all, or at any rate must be very weak. Experimental particulars are given in Part II.

These various differences between X-ray spectra and optical spectra need not be surprising in view of the fundamental differences which exist (in spite of analogies) between the origins of the two types of spectra. This difference is due to the fact that in the emission of the optical spectrum we have to do with the change of the motion of an electron whose orbit is characterized by higher quantum numbers than the orbits of the other electrons in the atom. In the emission of the X-ray spectrum, however, we meet with a change in the motion of an electron which must be expected to be in intimate interaction with the electrons of the same shell moving in orbits with the same quantum numbers *.

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* Compare Bohr, *Zeitschr. f. Physik*, ix. p. 1 (1922).

PART II.

The New Measurements of the L-*series in the X-ray Spectra of the Elements from* Rb *to* Ba *.

§ 1. As mentioned above, the results indicated by diagram I. have a direct bearing only on elements of atomic number comparable with that of niton. We should expect a change in this diagram for elements with lower atomic number, since the formation of new shells in the outer region of the atom with increasing atomic number must be accompanied by the appearance of new levels in the energy diagram which find their expression in the appearance of new lines.

My previous work was based on an investigation of the L-series of most of the elements from W to U †, which I carried out in the laboratory of Prof. Siegbahn. In view of a comparison with the theory of atomic structure, it was desirable to extend this investigation to elements of lower atomic number. In continuation of the former work I have therefore undertaken in the same laboratory an examination of the L-series of such elements. Though this work is not yet finished, the results already obtained seem to be sufficiently interesting to justify publication. In the present paper only the results obtained for the elements Rb–Ba will be discussed.

§ 2. The apparatus used for the experiments consisted of an X-ray vacuum-spectrograph, and the metal X-ray tube of the Coolidge type described by Prof. Siegbahn ‡. The tube was driven by two similar induction-coils of medium size. The primaries of the coils were connected in series to a source of alternating current of 50 cycles. As the tube itself acts as a current rectifier, no other rectifier was used in the secondary circuit. For most of the work the secondaries of the coils were connected in series. In this way a current of about 30 m.a. with a maximum tension of about 30 k.v. could easily be obtained. This tension is at the same time about the highest which can be sustained by this tube.

The tension was estimated by an adjustable parallel spark-gap. If the vacuum is not very good, the discharges through the tube give rise to great fluctuations in the tension. Under these circumstances no simple relation exists between the maximum tension measured by the spark-gap and the mean value. For a very high vacuum, which could be obtained easily with the molecular pump, the maximum tension was

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* Part of these experimental results have recently been published in *Archives Néerlandaises* (Serie III. A, tome vi., 1re livraison, p. 76.)

† *Zeitschr. f. Physik,* iv. p. 178 (1921), and *Zeitschr. f. Phys.* I. and II.

‡ Phil. Mag. xxxvii. p. 601 (1919).

about 1·4 times the mean tension. Up to 10 k.v. a Braun electrometer was used. At times it was necessary to work with a rather low tension. In this case the secondaries were connected in parallel, so that a larger current could be obtained. In photographing the absorption discontinuities of silver a maximum tension of not more than 5400 v. was used, and with this tension the influence of the "space charge" in limiting the magnitude of the maximum current could readily be observed. As is known, this effect has been experimentally and theoretically studied by Langmuir *, who clearly showed that in an extremely high vacuum the charge due to the electrons moving in the field between the hot wire cathode and the anode diminishes the rate at which electrons may escape from the hot wire and enter the field. For every tension there exists a maximum "saturation current" which depends on the dimensions of the tube and is independent of the temperature of the hot wire, if once a certain temperature has been surpassed. In this experiment the saturation current was less than 10 m.a. for a tension of about 5400 volt. As with this small current a very long exposure is required, it was desirable to get rid of the space-charge effect. This may be done by working with a somewhat lower vacuum, as in this case the positive ions of the gas neutralize the influence of the electrons in the field. Fortunately I was able to reduce the vacuum just sufficiently by an imperfectly sealed join in the tube. Otherwise it would have been necessary to lower the vacuum by regulating the speed of the molecular pump. Under these circumstances it was possible to get a current of about 50 m.a. at a tension of 5400 v.

As fairly long wave-lengths were measured, it was necessary to have also a vacuum in the spectrograph. The spectrograph was exhausted by a Gaede pump which gave a pressure of about 0·1 to 0·2 mm. The slit of the X-ray tube, which was immediately connected with the spectrograph, was covered with goldbeater's skin in order to separate the high vacuum from the low vacuum. This goldbeater's skin was coloured with erythrosine to prevent the visible light as much as possible from entering the spectrograph. The tube itself was exhausted by a molecular pump in series with the low vacuum pump. The pumps were able to give a very good vacuum in about 10 minutes. The time of exposure for one plate varied from $\frac{1}{2}$ to $1\frac{1}{2}$ hour.

§ 3. To get also the fainter lines of the spectrum, it appeared to be advantageous to use tensions several times higher than the critical exciting tension. Thus in several cases the maximum tension obtainable with the apparatus

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* Phys. Rev. II. ii. p. 450 (1913).

was used. On the other hand, the high tension gave some trouble in identifying the lines, as several lines due to other elements appeared in higher orders on the plates (*e.g.*, on many plates taken with a gypsum crystal, Cu K-lines and W L-lines were obtained in as high as the 5th order). In general, the best plates were obtained when the element could be placed in the form of a metallic sheet on the anticathode. For this reason Sb, Sn, In, and Cd were melted in a fairly pure state on the copper anticathode, while the elements Ag, Pd, and Rh were attached with solder ; Mo was pressed in a copper ring which was soldered on to the anticathode. There was no particular difficulty in obtaining good plates with these elements.

The other elements examined on this occasion (*i. e.*, Ba, Cs, Te, Ru, Nb, Zr, Y, Sr, and Rb) were used in the form of salts or oxides, which were pressed into the roughened surface of a copper plate soldered on to the anticathode. For every element this copper plate was renewed. As the salts are sputtered from the anticathode somewhat quickly, it appeared to be better not to use the highest energy which could be obtained from the apparatus. In general, for these elements the best plates were obtained with a maximum tension of about 20–25 k.v. and a current of not more than 15 m.a. For each element from 6 to 10 different plates were taken through the whole region of the spectrum. Between two exposures the tube was opened and a fresh quantity of salt was brought on the anticathode. Very often it was necessary to take several plates of the same part of the spectrum before a good one was obtained.

§4. The distances of the lines on the plates were measured under the microscope, and from this the wave-lengths of the new lines could be measured relatively to the lines α_1, β_1, and γ_1 which have previously been determined with great precision by Hjalmar *. The other lines mentioned by Hjalmar (α_2, α_3, β_4, β_3, β_2, and in a few cases γ_2, γ_3, γ_4) were usually determined by this author either relatively to α_1, β_1, γ_1, or from the old measurements of Friman, a correction having been applied.

In the following tables the lines determined by Hjalmar by the precision method as well as those measured relatively to them on his own plates have been taken from this author without change. These comprise nearly all the lines whose wave-lengths appear in his tables to one or two decimal places. The other lines have been determined in the present investigation.

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* *Zeitschr. f. Physik*, iii. p. 262 (1920), and vii. p. 341 (1921).

TABLE I.

Wave-lengths in X.U. (10^{-11} cm.).

	l	η	α_2	α_1	β_1	β_4	β_3	β_6	β_2	γ_5	γ_1	γ_2	γ_3	γ_4
37 Rb......	......	8029·0	......	7302·7	7060·4	6802·8	6769·9	6967·5		6738·6		6028·2		
38 Sr	7821	7505	......	6847·8	6609·2	6385·5	6349·9	6503·0		6278·8		5629·4		
39 Y	......	......	......	6434·9	6198·4	6001·9	5967·8	......		......		......		
40 Zr	6898	6593·1	......	6055·9	5822 8	5652·7	5618·2	5693·5	5573·4	5481·0	5373·0	4941·2		
41 Nb ...	6509	6195	5717	5711·3	5479·6	5331·4	5295·9	5346·1	5225·3	......	5024·1	4639		
42 Mo ...	......	5835	5400	5394·3	5165·8	5035·8	5000·2	......	4909·2	4819·0	4711·1	4361·3		
44 Ru......	......	......	4843·67	4835·67	4611·00	4512·6	4476·4	4476·4	4361·9	4276·6	4172·82	3887·9		
45 Rh......	5207·0	4911·2	4595·56	4587·78	4364·00	4277·8	4241·3	4230·1	4122·1	4035·2	3935·7	3677·0		
46 Pd......	4939·6	4650·2	4366·60	4358·50	4137·30	4062·3	4025·7	4007·0	3900·7	3811·6	3716·36	3480·9		
47 Ag......	4697·6	4410·1	4153·82	4145·64	3926·64	3861·1	3824·45	3799·4	3693·83	3607·3	3514·85	3299·7		
48 Cd......	4471·3	4187·5	3956·36	3947·82	3730·08	3674·25	3636·42	3607·3	3506·4	3418·1	3328·00	3131·6		
49 In	4259·3	3976·1	3772·42	3763·67	3547·83	3499·0	3461·9	3428·0	3331·2	3241·8	3155·29	2973·6		2919·1
50 Sn	4063·3	3781·8	3601·08	3592·18	3377·92	3336·3	3298·9	3262·2	3167·9	3077·4	2994·93	2827·3		2771·3
51 Sb	3880·3	3599·6	3440·75	3431·77	3218·36	3184·3	3145·14	3107·8	3016·6	2925·6	2845·07	2688·9		2633·6
52 Te	3710·1	......	3291·00	3281·99	3069·97	3040·0	3001·3	2964·4	2876·1	2783·1	2706·47	2564·9		2505·7
55 Cs	......	2983·3	2895·60	2886·10	2677·84	2660·5	2622·93	2587·5	2506·4	2411·1	2342·52	2232·2	2227·0	2169·1
56 Ba......	3128·7	2857·1	2779·02	2769·64	2562·24	2549·8	2511·0	2477·2	2399·3	2302·3	2236·60	2134·0	2129·5	2071·5

TABLE II.

Frequencies in multiples of the Rydberg number (109737 cm.$^{-1}$).

	l	η	α_2	α_1	β_1	β_4	β_3	β_6	β_2	γ_5	γ_1	γ_2	γ_3	γ_4
37 Rb......	......	113·50	......	124·78	129·06	133·96	134·61	130·75		135·23		151·17		
38 Sr	116·51	121·43	......	133·07	137·87	142·71	143·51	140·13		145·13		161·88		
39 Y	......	......	......	141·61	147·01	151·83	152·70	......		......		......		
40 Zr	132·07	138·22	......	150·47	156·50	161·21	162·20	160·05	163·50	166·26	169·63	181·42		
41 Nb	139·29	147·09	159·40	159·55	166·29	170·93	172·07	170·45	174·39	......	181·38	196·43		
42 Mo......	......	156·16	168·75	168·93	176·40	180·96	182·24	......	185·62	189·10	193·42	208·94		
44 Ru	......	......	188·13	188·44	197·62	201·94	203·57	203·57	208·91	213·08	218·38	234·38		
45 Rh......	175·01	185·55	198·29	198·62	208·77	213·03	214·86	215·42	221·07	225·83	231·53	247·83		
46 Pd	184·48	195·96	208·69	209·07	220·25	224·32	226·36	227·42	233·62	239·08	245·19	261·80		
47 Ag	193·99	206·63	219·37	219·80	232·06	236·01	238·27	239·85	246·69	252·62	259·15	276·17		
48 Cd	203·80	217·61	230·32	230·82	244·29	248·00	250·59	252·62	259·89	266·60	273·81	291·00		
49 In	213·95	229·18	241·55	242·12	256·84	260·43	263·22	265·84	273·55	281·10	288·79	306·45		312·18
50 Sn	224·27	240·96	253·05	253·67	269·76	273·13	276·24	279·34	287·66	296·11	304·26	322·31		328·82
51 Sb	234·85	253·16	264·84	265·53	283·13	286·18	289·73	293·22	302·08	311·48	320·29	338·90		346·01
52 Te	245·62	......	276·89	277·65	296·83	299·75	303·61	307·41	316·84	327·44	336·69	355·28		363·69
55 Cs	......	305·45	314·70	315·74	340·29	342·50	347·41	352·18	363·58	377·94	389·00	408·23	409·18	420·11
56 Ba	291·26	318·95	327·90	329·01	355·64	357·38	362·89	367·86	379·80	395·81	407·42	427·03	427·92	439·91

TABLE III.

$\sqrt{\frac{\nu}{R}}$ (square roots of frequencies).

	l	η	α_2	α_1	β_1	β_4	β_3	β_6	β_2	γ_5	γ_1	γ_2	γ_3	γ_4
37 Rb……	……	10·653	……	11·170	11·360	11·574	11·602	11·436		11·629		12·295		
38 Sr ……	10·794	11·019	……	11·536	11·742	11·946	11·979	11·838		12·047		12·723		
39 Y ……	……	……	……	11·900	12·125	12·322	12·357	……		……		……		
40 Zr ……	11·492	11·756	……	12·267	12·510	12·697	12·736	12·651	12·787	12·894	13·030	13·580		
41 Nb……	11·832	12·128	12·625	12·631	12·895	13·074	13·118	13·056	13·206	……	13·468	14·015		
42 Mo……	……	12·497	12·990	12·998	13·282	13·452	13·500	……	13·624	13·751	13·908	14·455		
44 Ru……	……	……	13·716	13·727	14·058	14·211	14·268	14·268	14·454	14·597	14·778	15·309		
45 Rh……	13·229	13·622	14·081	14·093	14·449	14·595	14·658	14·677	14·868	15·028	15·216	15·745		
46 Pd……	13·582	13·999	14·446	14·459	14·841	14·978	15·045	15·080	15·285	15·462	15·658	16·180		
47 Ag……	13·923	14·374	14·811	14·826	15·233	15·363	15·436	15·487	15·706	15·894	16·098	16·618		
48 Cd……	14·277	14·752	15·176	15·193	15·630	15·748	15·830	15·894	16·121	16·328	16·547	17·059		
49 In ……	14·627	15·139	15·542	15·560	16·026	16·138	16·224	16·304	16·539	16·766	16·994	17·506		17·668
50 Sn ……	14·976	15·523	15·907	15·927	16·424	16·527	16·620	16·713	16·960	17·208	17·443	17·953		18·133
51 Sb ……	15·325	15·911	16·274	16·295	16·827	16·917	17·021	17·124	17·381	17·649	17·897	18·409		18·602
52 Te ……	15·672	……	16·640	16·663	17·229	17·313	17·425	17·533	17·800	18·095	18·349	18·849		19·071
55 Cs ……	……	17·477	17·740	17·769	18·447	18·504	18·639	18·767	19·068	19·440	19·723	20·211	20·228	20·497
56 Ba ……	17·066	17·859	18·108	18·139	18·858	18·904	19·050	18·180	19·488	19·895	20·185	20·655	20·687	20·974

Hjalmar and Friman found β_4, β_3, and β_2 as far down as Pd, γ_1 appears for the last time for Mo in their tables, and the η-l and γ_5-β_6 doublets were not observed at all in this region. But I could still detect β_4 and β_3 for Sr and Rb, β_2 and γ_1 were found as far down as Zr, although very faint (Hjalmar's value of $\lambda=5295{\cdot}1$ for Nbβ_2 corresponds to my value of $\lambda=5295{\cdot}9$ X.U. for β_3 for the same element). The lines γ_2, γ_3, and γ_4 in this region had not been identified correctly by the former authors. The line $\gamma_{2,3}$ (γ_2 and γ_3 could no longer be separated in this region) has still been observed for Rb and γ_4 still for In. Both doublets η–l and γ_5–β_6 could also be measured down to Rb and Sr.

The spectra of the elements Ba and Cs were taken with a rocksalt crystal, Te–Pd with calcite, Rh partly with calcite, partly with gypsum, and Ru–Rb with a gypsum crystal. For these elements the breadth of the lines was considerably greater than the width of the slit, implying that the lines represent a finite frequency interval. Strongly exposed lines obtained with a rocksalt or calcite crystal, especially, were diffuse at the edges, which obviously reduced the accuracy of the measurements. Extremely broad and diffuse were the lines, η, l, and $\gamma_{2,3}$. For β_2 for some elements a broadening could be observed at the short wave-length side. The lines α_1 and β_1 were accompanied by satellites (see Part II. § 7), while for the lightest elements α_2 could not be separated from α_1. All this reduced the accuracy of the measurements. Usually only reference measurements were made. The distance on the plate to the reference line was often fairly large, sometimes over 10 mm., and in a few cases even between 15 and 20 mm. Thus errors in the measurements of the line-distances and irregularities in the structure of the crystal may be quite appreciable here. In the case of the lines taken with a rocksalt or calcite crystal, however, the error in the wave-lengths must be in nearly all cases considerably smaller than one X.U. This is especially true of the lines lying in the neighbourhood of a reference line. In a few cases (sometimes for η, l, and $\gamma_{2,3}$) this error may be a little larger. Some lines could not be measured under a microscope and their distance was estimated with a millimetre scale. They stand in the tables without decimals in the wave-lengths. Their errors may be more than 2 X.U. Using gypsum as analysing crystal, we have on the one hand the disadvantage of the greater space-lattice constant, on the other hand the advantage of getting sharper lines, which usually lie nearer together on the photographic plate. For the lines measured with a gypsum crystal we have to multiply the above given limits of error by $1\frac{1}{2}$–2. Thus far I have neglected the errors in the wave-length which are due to the remarkable fact detected by Stenström † that Bragg's relation $n\lambda = 2d \sin \phi$ is only approximately true. Especially with a gypsum crystal the deviations are fairly large and may give rise to an error of several X-units, but as this error is nearly the same for wave-lengths of about the same value it does not affect the conclusions drawn in this paper. Tables I., II., III. contain only the lines which can be arranged in diagram I.

§ 5. The right classification of the lines often gives trouble. Some indications were supplied by the relativity L-doublets, which are given in Table IV. Down to Ag the γ_1-β_2 doublet difference is apparently smaller than the other ones ‡, lower down this "doublet defect" disappears in the accidental errors. The cause of this defect will be seen from diagram I. The pairs of lines η-l, β_1-α_2, and γ_5-β_6 come each from the same initial level, whereas γ_1 and β_2 come from different initial levels. I have never observed the transition N_4–L_1,

TABLE IV.

Relativity L-doublets.

	η–l.	β_1–α_2.	γ_5–β_6.	γ_1–β_2.	L_1–L_2.
37 Rb	...	4·28*	4·48		
38 Sr	4·92	4·80*	5·00		
39 Y	...	5·40*	...		
40 Zr	6·15	6·03*	6·21	6·13	
41 Nb	7·10	6·89	...	6·99	
42 Mo.........	...	7·70	...	7·80	
44 Ru	...	9·49	9·53	9·47	
45 Rh	10·54	10·48	10·41	10·46	
46 Pd	11·48	11·56	11·66	11·57	
47 Ag	12·64	12·69	12·77	12·46	12·68
48 Cd	13·81	13·97	13·98	13·92	
49 In	15·23	15·29	15·26	15·24	
50 Sn	16·69	16·71	16·77	16·60	
51 Sb	18·31	18·29	18·26	18·21	
52 Te	...	19·94	20·03	19·85	
55 Cs	...	25·59	25·76	25·42	(25·8)
56 Ba	27·69	27·74	27·95	27·61	28·00

* As α_2 could not be measured for this element, the value β_1–α_1 has been used. This value is smaller than β_1–α_2.

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† Stenström, Dissertation, Lund, 1919; Hjalmar, *Zeitschr. f. Phys.* i. p. 439 (1920); Siegbahn, *Comptes Rendus*, clxxiii. p. 1350 (1922).

‡ Compare also *Zeitschr. f. Phys.* II. table 3, p. 191.

which might be supposed to exist by analogy with the transition M_2–L_1, which gives rise to the line α_2.

Pairs of lines the frequencies of which show a relativity doublet difference occur very often in the X-ray spectrum, but those which would form a screening doublet do not occur at all in virtue of the *a*-*b* rule (see diagram I.). But we may find lines the frequency difference of which is either the sum or the difference of two screening doublets. To the former class belong $\beta_4-\eta$ and $\gamma_2-\gamma_5$, to the latter $\beta_3-\beta_1$ and $\gamma_3-\gamma_1$. As the screening doublets are approximately proportional to the effective nucleus charge of the atom, the differences of the square roots of the frequencies of these lines are easily seen to be nearly constant for the different elements. These differences are shown in Table V. This table in connexion with Table IV. most strongly supports the identification of the lines which has been proposed by the author. The differences $\beta_4-\eta$ and $\gamma_2-\gamma_5$ increase slowly with increasing atomic number. This is due to the fact, that in every line-frequency the screening constant of the initial as well as that of the final level is involved, and these screening constants in general will be different. For the heaviest elements the relativity correction here also plays a part.

TABLE V.

Differences in $\sqrt{\frac{\nu}{R}}$.

	$\beta_4-\eta$	$\gamma_2-\gamma_5$	$\beta_3-\beta_1$	$\gamma_3-\gamma_1$
37 Rb	0·921	0·666	0·242	
38 Sr	927	676	237	
39 Y	...	...	232	
40 Zr	941	686	226	0·550
41 Nb	946	...	223	547
42 Mo	955	704	218	547
44 Ru	...	712	210	531
45 Rh	973	715	209	527
46 Pd	979	718	204	522
47 Ag	989	724	203	520
48 Cd	996	731	200	512
49 In	999	740	198	512
50 Sn	1004	745	196	510
51 Sb	1006	760	194	511
52 Te	...	756	196	510
55 Cs	1027	771	192	505
56 Ba	1045	770	192	502
74 W	1136	822	202	517
83 Bi	1200	910	224	495

The values which I have given for γ_3 may be verified by some measurements in the K-series. As is seen from diagram I. the following relation must hold for the frequencies :

$$K\beta_2 - K\beta_1 = L\gamma_3 - L\beta_3.$$

Table VI. gives some numerical values.

TABLE VI.

	$L\gamma_3$-$L\beta_3$.	$K\beta_2$-$K\beta_1$.
Cd	40·41	39·0
Pd	35·44	32·4
Rh	32·97	34·7
Mo	26·70	26·5

The values for the K-lines of Rh and Mo are calculated from the wave-lengths given by Duane * ($K\beta_2$ is called $K\gamma$ by Duane). The values for Cd and Pd have been kindly furnished me by Mr. A. B. Leide, who has measured some K-lines in this laboratory. As an error of 0·5 X.U. in one of the K-lines involves an error of more than 4 per cent. in the differences under consideration, we may say that the agreement is very good.

The line β_6 crosses β_4 and β_3 twice, a circumstance which in the beginning gave rise to some difficulties in the identification of these lines. β_6 crosses β_4 once for Pt and β_3 for Dy and crosses both lines again between Rh and Mo. In this region the β_6-curve is nearly a straight line in the Moseley-diagram, whereas the β_3- and β_4-lines are noticeably curved.

§ 6. As regards the intensities of the different lines, it has been found that for the elements U–W the lines β_3 and β_4 are not much different in intensity, but in the region Ba–Rb β_3 is much more intense than β_4. An illustration of this fact is given by figs. 1 and 2 (Pl. XXIII.) †. Fig. 1 gives

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* Phys. Review, II. xiv. p. 373 (1919).

† The reproductions are about twice the natural size. The black lines in the original photographs are represented as white lines in the reproductions.

the lines of the β-group for Pb taken with a rocksalt crystal; fig. 2 gives nearly the whole L-spectrum of Rh* taken with a gypsum crystal. For the lines γ_2 and γ_3 the case is much similar: for the heaviest elements they are approximately of equal intensity; for Ta γ_3 seems to be prominent; for Ba and Cs γ_3 is still fairly strong, whereas γ_2 can scarcely be perceived. This fact may imply that the disturbances of the inner atomic field which give rise to β_4 and γ_2 (the azimuthal quantum number does not change for these lines) are less important for the lighter elements. But the change of relative intensity of β_3 and β_4 must partly be accounted for as a change in the intensity of β_3. This line seems to correspond to a transition less probable for the heavier elements than for the lighter ones.

In the case of η–l and γ_5–β_6 doublets a corresponding change of the intensities could not be observed. For all elements l is about 2–3 times as strong as η and β_6 2–3 times as strong as γ_5. The lines η and γ_5 like β_4 and γ_2 correspond to transitions for which the azimuthal quantum number does not change; the lines l and β_6 correspond to transitions for which the azimuthal quantum number decreases, whilst the lines β_3 and γ_3 correspond to transitions for which it increases.

§ 7. Another interesting result of this investigation of the L-spectra of the lighter elements was the discovery that the two most intense lines of this spectrum, α_1 and β_1, show a complicated structure, which has not been observed for the heavier elements, or is at any rate much less pronounced. Both lines in question show a broadening on the short wave-length side. This cannot be ascribed to any peculiarity in the experimental conditions, as it has a very regular structure which is independent of the time of exposure. On the other hand, the line β_3 which on several long exposed plates was very intense showed no such structure, appearing merely somewhat diffuse on both sides. For the α_1-line this broadening ends fairly abruptly, so that the edge could be measured with sufficient accuracy. From this the wave-length corresponding to this edge could be calculated. (A correction must be made for the half width of the slit.) In the following tables this wave-length has been called α_1'. This must be

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* The satellites of α_1 and β_1 (see Part III. § 7) have not been well reproduced on this plate. They were more easily visible on the original photograph. On the reproduction Sn Lα stands erroneously for Fe Kα 2nd order.

understood to mean that there is an emission-band extending from α_1 to α_1'. When one passes from Cd to Ag this band suddenly changes. For Ag two new lines could be detected: one, which is within this emission-band, is called α_3, the other, a short distance outside, is called α_4 *. The intensity of the line α_3 changes very little from Ag, where it is found for the first time, down to Rb. The line α_4 seems to become somewhat stronger for the lighter elements †.

The satellites of β_1 take a different course. The proximity of β_4 makes it impossible to study these satellites for the elements Ba and Cs, but from Sb (where they were observed for the first time) down to Rb they do not essentially change. Firstly there is an emission band, the short wave-length-edge of which has been denoted by β_1'. This band is fainter than the α_1-band and not so sharply limited. Furthermore, outside the band a line has been found, denoted by β_{13}, which is faint for the elements Sb–Rh, but becomes more intense for the elements Mo–Rb.

It is a well known fact that the human eye does not always form a correct judgment of the blackening of a photographic plate. In particular a sudden change in the *gradient* of the blackening gives the impression of a white or a black line. It therefore seemed to be advisable to study the α_1- and β_1-satellites with the photometer also ‡. It must be borne in mind, however, that even the photometer does not give a wholly correct impression of the blackening of the plate. With this photometer part of the photographic plate is projected by a microscope-objective on the slit of the thermopile. In these measurements 0·03 mm. on the photographic plate corresponds to the breadth of the slit. Further, it is impossible to have a sharp image for the

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* (Note added during the proof.)—Recently, however, by taking some other powerfully exposed plates, I was able to establish the existence of the lines α_3 and α_4 for Cd also, but for this element they are very faint. For In the existence of these lines remains very uncertain, for Sn no trace of them could be observed. In this connexion it might be of interest to remark that the appearance of these satellites is within wide limits independent of the tension used on the tube.

† I have previously observed the broadening of α_1 for the elements Ta–U, but have interpreted it erroneously. See *Zs. f. Phys.* II. p. 191.

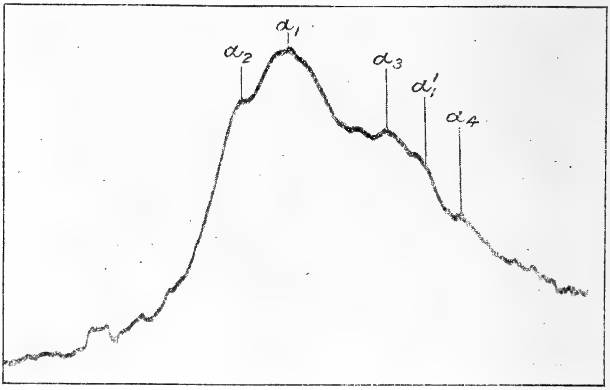
‡ This photometer has been described by M. Siegbahn, *Ann. der Physik*, (4) xlii. p. 689 (1913), and A. E. Lindh, *Zs. f. Phys.* vi. p. 303 (1921), See also W. J. H. Moll, Proceedings Phys. Soc. London, vol. xxxiii. part 4, p. 207 (1921).

visible and the infra-red light at the same time. Hence a blackening, which may be represented thus :  is registered by the photometer thus :  *.

Small irregularities of the plate which are not readily noticed by the eye are registered by the photometer. Most of the small abrupt changes of the curves must be explained in this way. As a rule the more continuous changes correspond to changes in the blackening of the plate. This may be verified by comparing photometer-curves taken across the plate at different heights.

Fig. 1 gives a typical curve for Rh (taken in the opposite direction as compared with the other curves). Fig. 2 shows the great difference between the Rh † α_1 and the In α_1 line. Fig. 3 clearly demonstrates that this difference suddenly appears between Cd and Ag. (The numerous accidental

Fig. 1.



Rhodium Lα_1 with satellites (calcite crystal).

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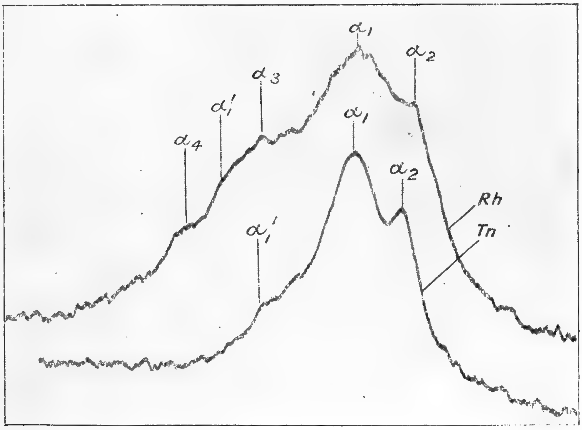
* Another question is, whether the blackening of the plate really gives a correct impression of the emission-spectrum. It might be supposed, that for these strongly exposed lines the secondary radiation in the photographic plate has some effect in broadening the lines, but as the breadth of the lines largely depends on the space-lattice constant of the analysing crystal (with gypsum rather sharp lines were obtained) we may conclude that this influence cannot be very great.

† This curve is taken at a height different from that in fig. 1. In figs. 2, 3, and 4 *Tn* stands for *In*.

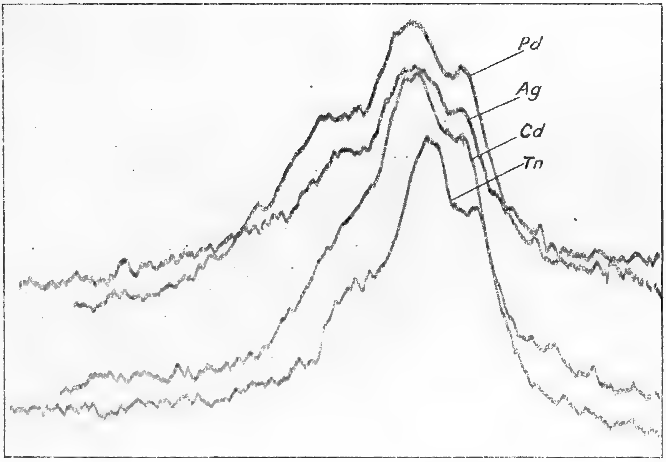
irregularities in the latter curves must be ascribed to some mechanical disturbance.) Fig. 4 gives the β_1 curves for Ag

Fig. 2.



Rh $L\alpha_1$ and In $L\alpha_1$ with their satellites (calcite crystal).

Fig. 3.

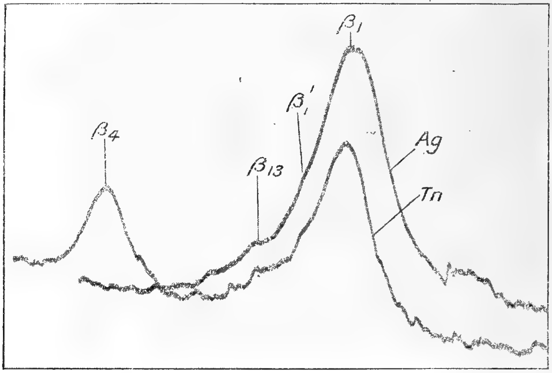


The $L\alpha_1$ lines of Pd, Ag, Cd, and In, with their satellites (calcite crystal).

and In ; β_1' and β_{13} are much less pronounced than the α_1 satellites. No sudden change is here observed for Ag.

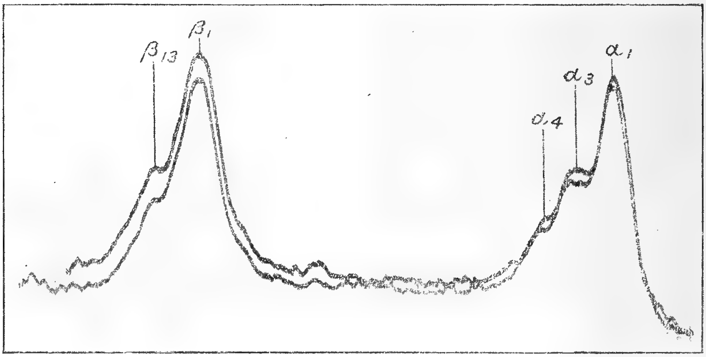
Fig. 5 shows α_1 and β_1 with their satellites for Zr, taken at two different heights of the plate. On the plates of the elements Mo–Rb taken with a gypsum crystal, α_3 could not be separated from α_1'. This gives a somewhat asymmetrical form to this line. α_2 and β_1', which could be detected easily with the eye, could not be separated from α_1 and β_1 with the photometer. Fig. 3 (Pl. XXIII.) gives a reproduction of the α_1- and β_1-lines of Rb.

Fig. 4.



Ag Lβ_1 and In Lβ_1 with their satellites (calcite crystal).

Fig. 5.



Zr Lα_1 and Lβ_1 with their satellites (gypsum crystal).

The wave-lengths and frequencies of the α_1- and β_1-satellites are given in Tables VII., VIII., and IX. The wave-lengths of α_3 for Mo–Rb are probably too great, since this line

TABLE VII.

	β_{13}			β_1'		
	λ	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\beta_{13}}}{R}}-\sqrt{\frac{\nu_{\beta_1}}{R}}$	λ	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\beta_1'}}{R}}-\sqrt{\frac{\nu_{\beta_1}}{R}}$
37 Rb	7022·4	129·77	0·032	7041	129·42	0·016
38 Sr	6573·4	138·63	32	6590	138·28	17
40 Zr	5793·3	157·30	32	5807	156·93	17
41 Nb	5449·7	167·21	36	5465	166·76	18
42 Mo	5138·4	177·34	35	5150	176·95	20
45 Rh	4342·5	209·85	37	4351	209·45	23
46 Pd	4117·1	221·33	36	4125	220·91	22
47 Ag	3906·9	233·24	39	3914	232·84	26
48 Cd	3711·6	245·52	39	3719	245·04	24
49 In	3530 4	258·12	40	3539	257·48	20
50 Sn	3360·7	271·15	43	3367	270·64	27
51 Sb	3202·6	284·54	41	3210	283·91	23

TABLE VIII.

	α_4.			α_3.		
	λ	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\alpha_4}}{R}}-\sqrt{\frac{\nu_{\alpha_1}}{R}}$	λ	$\frac{\nu}{R}$	$\sqrt{\frac{\nu_{\alpha_3}}{R}}-\sqrt{\frac{\nu_{\alpha_1}}{R}}$
37 Rb	7248·8	125·71	0·042	7271·0	125·33	0·025
38 Sr	6797·3	134·06	43	6818·3	133·64	24
40 Zr	6013·2	151·54	43	6029·1	151·14	27
41 Nb	5671·1	160·68	45	5684·9	160·30	30
42 Mo	5356·4	170·13	45	5370·3	169·68	28
45 Rh	4558·8	199·89	45	4571·3	199·34	26
46 Pd	4330·9	210·41	46	4342·7	209·84	27
47 Ag	4119·4	221·21	47	4131·0	220·59	26

TABLE IX.

	α'_1.		
	λ.	$\frac{\nu}{R}$.	$\sqrt{\frac{\nu_{\alpha_1'}}{R}}-\sqrt{\frac{\nu_{\alpha_1}}{R}}$.
45 Rh	4564·9	199·62	0·036
46 Pd	4336·2	210·15	38
47 Ag	4125·4	220·90	36
48 Cd	3928·8	231·95	37
49 In	3744·7	243·35	40
50 Sn	3574·0	254·97	41
51 Sb	3413·8	266·94	43
55 Cs	2870·8	317·43	47
56 Ba	2755·1	330·76	48

could not be separated from α_1'. The last columns give the difference between the square root of the frequency of α_1 or β_1 and that of a satellite. These differences are nearly constant but decrease slowly with decreasing atomic number.

§ 8. Two very remarkable lines are the new lines β_{11} and β_{12}. They may be seen on fig. 2 (Pl. XXIII.). For Ba, Cs, Te, these lines probably do not occur; they could be detected for the first time for Sb. From In down to Mo they are fairly strong lines which could be easily measured under the microscope. They could be detected also for Nb and Zr, although for these elements they nearly coincide with γ_5, which is a much sharper line in this region. For Sr and Rb they are very faint or perhaps they do not occur at all. Apparently these lines have nothing to do with the lines β_7, β_8, β_9, and β_{10} which I have previously measured for the heavier elements *.

On the short wave-length side of γ_1 a new line (γ_7) could be detected. This line is weaker than β_{11} and β_{12} and could be observed as early as Ba. It might be supposed that this line forms a relativity-L-doublet with β_{11} or β_{12}. The differences, however, between the frequency-differences $\gamma_7-\beta_{11}$ or $\gamma_7-\beta_{12}$ and the $\beta_1-\alpha_2$ doublet are in most cases greater than the limits of experimental error. As is seen from the last columns of Table X., β_{11} and β_2 form a screening-doublet, also β_{12} and β_2. The same is true for γ_7 and γ_1. Some other

TABLE X.

	Wave-lengths.			Frequencies.			Differences $\sqrt{\frac{\nu}{R}}$.		
	β_{11}	β_{12}	γ_7	β_{11}	β_{12}	γ_7	$\beta_{11}-\beta_2$	$\beta_{12}-\beta_2$	$\gamma_7-\gamma_1$
41 Nb......	5161		......	176·56		......	0·081		
42 Mo......	4859·7	4841·7	......	187·52	188·21	......	0·071	0·095	
45 Rh......	4084·8	4072·5	5896·8	223 09	223·76	233·85	68	91	0·076
46 Pd......	3867·6	3856·7	3676	235·61	236·28	247·87	65	86	86
47 Ag......	3663·3	3653·7	3479·5	248·76	249·40	261·89	66	87	85
48 Cd.....	3477·5	3468·4	3302	262·05	262·73	275·98	67	88	66
49 In	3304·0	3295·9	3125	275·81	276·48	291·57	68	89	81
50 Sn	3142·6	3134·7	2968·5	289·97	290·69	306·98	69	90	78
51 Sb	2993·4	2985·8	......	304·43	305·20	......	67	89	
56 Ba	......		2218	......		410·82	......		84

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* (Note added during the proof.)—From a paper recently published by Mr. Wentzel (*Annalen der Physik*, lxvi. p. 437 (1921)), however, we are inclined to suppose that the lines β_{11} and β_{12} might be connected with the line β_8 of the heavier elements.

new lines, which possibly may exist for some elements (one between β_6 and β_2 and one between α_1 and β_1) will be studied in connexion with an investigation of the elements Ta–Ba and Rb–Cu.

§ 9. Tables XI. and XII. give the characteristic absorption discontinuities in the L-region for Ba, Cs and Ag, and the shortest wave-lengths of the emission spectrum which belong to each of them. The absorption wave-lengths of Ba and Cs were accidentally found on the same plates on which the emission spectra were taken. They were obviously due to the selective absorption of the heterogeneous radiation of the copper anticathode, in the Ba and Cs salt used on the anticathode. Hertz's values * are added in parenthesis. They differ from ours by about 7 X.U. in the mean. The absorption spectrum of Ag is determined with a gypsum crystal,

TABLE XI.

Wave-lengths.

	L_1	β_2	L_2	γ_1	L_3	γ_3	γ_4
56 Ba	2356·7 (2348)	2399·3	2198 (2194)	2236·60	(2063)	2129·5	2071·5
55 Cs	2466 (2459)	2506·4	(2299)	2342·52	(2157)	2227·1	2169·4
47 Ag	3684·4	3693·83	3504·7	3514·85	3260·5	3299·7	

TABLE XII.

Frequencies $\frac{\nu}{R}$.

	L_1	β_2	L_2	γ_1	L_3	γ_3	γ_4
56 Ba	386·67 (388·1)	379·80	414·67 (415·3)	407·42	(441·7)	427·92	439·91
55 Cs	369·50 (370·6)	363·58	(396·4)	389·00	(422·5)	409·18	420·11
47 Ag	247·33	246·69	260·01	259·15	279·48	276·17	

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* *Zeitschr. für Physik*, iii. p. 19 (1920).

making use of the increased absorption in the silver of the photographic plate. For this region of wave-lengths, especially if the rather faint discontinuity L_3 is to be photographed, it is desirable to exclude totally the spectra of higher order. For this reason the maximum tension on the tube should be not more than twice the critical exciting tension. Therefore in taking the L_3 absorption the mean tension on the tube, as read with the Braun electrometer, was fixed at about 5400 volts. As a fairly large current was used (50 m.a.) a very good plate was obtained in four hours. The discontinuities L_1 and L_2 were both found on one plate after an exposure of about three hours.

§ 10. As has been stated in Part I. § 6, I have tried to obtain some experimental information about the existence of the line L_3L_1, *i. e.*, the transition L_1–L_3. For tungsten this line should lie in the M-region, between the lines $M\beta$ and $M\gamma$ which have been measured by Stenström. We may calculate the wave-length of this line for W from the following data. The frequency of the line L_3L_1 is equal to the frequency difference of the absorption discontinuities L_1 * and L_3 *. These have been measured by Duane and Patterson. They found 1213·6 and 1024 X.U. respectively. From this we find for the frequency difference L_3-L_1 139·07 in multiples of the Rydberg number, from which we may calculate the required wave-length as 6553 X.U. Taking into account the limits of experimental error given by Duane and Patterson, we find that the error in the wave-length in question must be less than 3 per cent. We may calculate the same wave-length with somewhat greater accuracy in the following way. From diagram I. we see that the following relation must hold between the frequencies :

$$L\beta_2+(L_3-L_1)=L\beta_3+M\gamma.$$

Putting into this formula the frequencies measured by Siegbahn for $L\beta_2$ and $L\beta_3$ and the value for $M\gamma$ measured by Stenström, we find for the same frequency difference L_3-L_1 139·05, giving the same wave-length 6553 X.U. Taking into account the limits of error of the $M\gamma$ line and of the L-lines, which can be measured with greater accuracy than the discontinuities, we find that the error in this value is less than 0·3 per cent.

We should expect that this line would only arise if an electron is removed from the L-shell in such a way that the

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* By these symbols the levels as well as the absorption-discontinuities corresponding to these levels are denoted.

remaining electrons form a configuration corresponding to a L_3-level. Using a tungsten anticathode, the tension on the tube must according to Einstein's relation be more than 12000 volt. As the expected line might not be very strong, it is desirable to work with a tension which is at least twice as great. The tube was therefore driven with the maximum tension which could be obtained. With this tension a very strong L-spectrum in the first order was obtained in ten minutes. As analysing crystal a gypsum crystal was used ; the time of exposure was one hour. Besides the lines $M\beta$ and $M\gamma$ several other lines which could not be identified at first sight were found on the plate. Now the lines in the M-series have a very typical structure, being rather diffuse and broadened on the short wave-length side. Therefore no doubt could arise as to the identification of these lines. As to the new line L_3L_1, however, we should expect that it would be distinctly different, and especially that it would be fairly sharp for W. For a right interpretation of the plate it was therefore desirable to exclude all the lines which appeared on the plate in higher order. This could be done in the following simple way. A new plate was exposed under the same conditions. Half of this plate was covered with an aluminium sheet of 7 μ thickness. By this sheet wave-lengths of more than 6000 X.U. are totally absorbed. Fig. 4 (Pl. XXIII.) gives a reproduction of the spectrum obtained in this way. Most of the lines are not appreciably absorbed by the aluminium, but the lines $M\beta$ and $M\gamma$ have been totally absorbed. Copper and tungsten lines were found in 4th and 5th order. Between the $L\beta_2$ and $L\beta_1$ line of W the line $L\beta_3$ was seen on the plate also in 5th order. This line comes from the L_3 level. As $L\beta_3$ is not a very strong line for W, it was very faint on the plate, and it cannot be seen on the reproduction. Further the Ca K absorption line in the second order may be seen as a dark line quite near the $M\gamma$ line of W. This line is due to the selective absorption in the Ca of the crystal *. From the appearance of the tungsten lines in such high order we may conclude that the experimental conditions were such as to excite the L_3 level quite sufficiently to give rise to the line L_3L_1, unless this transition is very improbable. The place where we should expect the line is marked with a ↑ on the reproduction. In the neighbourhood of this place only one very faint line was seen on the plate. This line, however, was not appreciably absorbed

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* In general, absorption discontinuities are obtained in a very easy manner if the absorbing element forms part of the analysing crystal.

by the aluminium sheet (the reproduction does not give a very good impression of this fact). It is quite possible that it is the tungsten Lγ_1 in the 6th order.

In the same way I was able to show that the transition L_2L_1 does not exist; this, however, is what we should already expect from the *a–b* rule.

Part III.

Discussion of Results.

§ 1. As has been stated in Part II. § 1, the object of this paper is to compare the changes in the characteristic X-ray spectrum as the atomic number decreases with the changes in the structure of the atom as given by Bohr's theory, of which a brief account has been given in Part I. In order to do this, we will deal with the diagrams of the energy levels of the inert gases, which are based upon measurements of the elements preceding or following the inert gases in the periodic table. For niton the diagram has already been given in Part I. of this paper.

As regards this diagram, the following remarks may here be made. Only the lines belonging to the L-series have been systematically investigated for the elements in the neighbourhood of niton *. The complexity of the line L_4 which is suggested by analogy with the appearance of the pairs of lines Lβ_3–Lβ_4 and Lγ_3–Lγ_2 could not be proved experimentally, because of the small difference of energy between the levels O_3 and O_4. The energy-difference between the levels O_1 and O_2 could not be obtained experimentally for the same reason. As yet there is no experimental evidence for the existence of the three P-levels inserted in the diagram. Perhaps the line 568·9 found by Dauvillier † in the spectrum of U represents a transition $P_1 \rightarrow L_3$. But since in general it is very dangerous to draw conclusions from the measurements of only one element, it seems better to postpone a discussion of the P-levels until a thorough investigation of the X-ray spectrum of the radioactive elements has been made. The K-spectrum of the elements in the region of high atomic number has been measured with sufficient accuracy for W only. But also different measurements of the K-series, made by several authors for elements of lower atomic number, support the arrangement of lines

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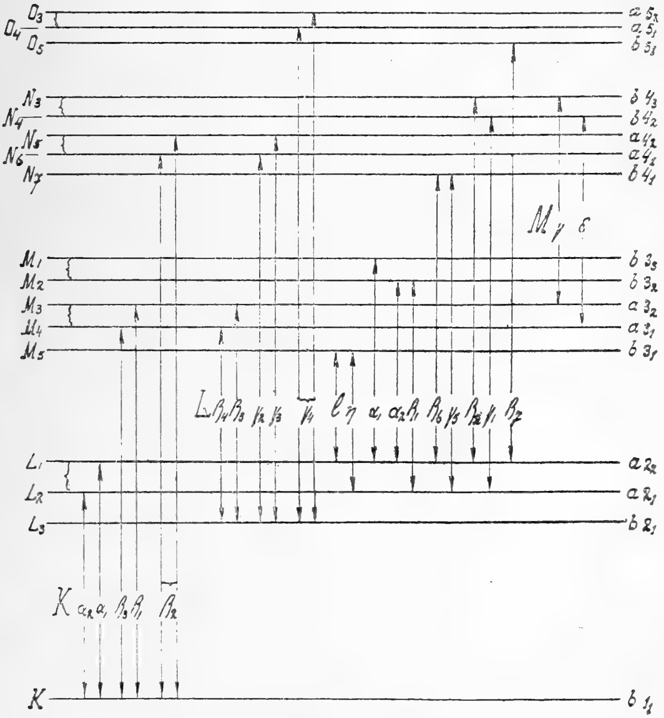
* See D. Coster, *Zeitschrift f. Physik*, iv. p. 178 (1921) and I. and II. In I. and II. the arguments are given in favour of the arrangement of the lines in the diagram 1.

† *Comptes Rendus*, clxxii. p. 1350 (1921).

given in the diagram. The line Kβ_3 has been detected by de Broglie * only for the elements tungsten and rhodium. The frequency-difference found by de Broglie for the lines Kβ_1 and Kβ_3 agrees very well with that for the lines Lβ_3 and Lβ_4. The complexity of the line Kβ_2 could not be observed but is suggested by analogy with the pairs of lines Kβ_1–Kβ_3, Lβ_3–Lβ_4, and Lγ_3–Lγ_2. In any case it is probable that most of the energy of this line is due to the transition $N_5 \rightarrow K$. The lines in the M-region have been measured by Stenström and Karcher for different elements. It is highly probable that there exist further transitions in this region, other than those detected by Stenström.

Diagram II.—Xenon.



§ 2. The diagrams II. and III. for the inert gases, xenon and krypton, are derived from the experimental results given in Part II. of this paper. As for the L-series we see from the tables in Part II. that all the lines inserted in the

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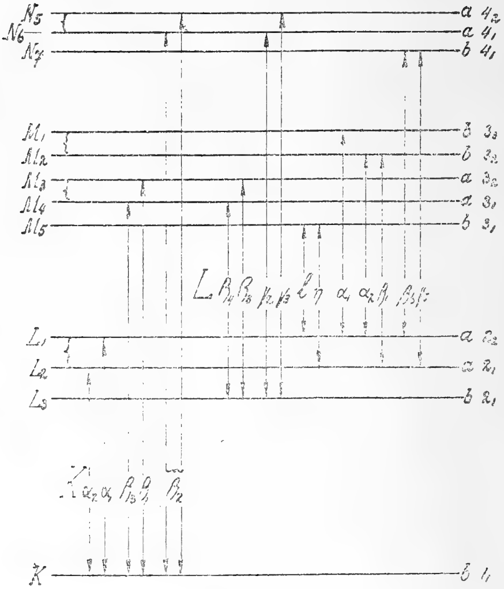
* *Comptes Rendus,* clxx. p. 1053 (1920) and clxx. p. 1245 (1920).

diagrams were actually measured for the elements with higher atomic numbers than xenon or krypton respectively. The single exception is the line $L\beta_7$. Though there are some indications that this line has been found for Ba and Cs, its identification is not quite certain. An investigation of the rare-earth metals, as yet unfinished, will possibly settle the question. The lines α_1, α_2, β_1 and β_2 of the K-series have been measured by several authors for different elements in this region; the line β_3, which lies at a very small wave-length distance from β_1, has been measured only for Rh, by de Broglie, as stated above. The lines $M\gamma$ and $M\delta$ have only been inserted in the xenon diagram for the sake of completeness. They have only been found for the elements U, Th, Bi, Pb, Au, and Pt* and they have not yet been studied systematically. It will be very difficult to measure them in this region, as even for Ba they should have wave-lengths of about 13000 and 12000 X.U. respectively. The largest wave-length hitherto measured with the aid of crystal reflexion is the line $L\alpha$ for copper (13309 X.U.).

Diagram III.—Krypton.



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* See Stenström, Dissertation, Lund, 1919; Karcher, Phys. Rev. II. xv. p. 285 (1920). These lines have been called $M\gamma_1$ and $M\gamma_2$ by Karcher.

On the other hand, we may see from a comparison of the diagrams I. and II. and the tables of Part II. that the lines, which according to the diagrams should fall out between niton and xenon (*i. e.* in the L-series β_5 and γ_6) were actually not found for the elements in the neighbourhood of xenon. In the same way we may see from the diagrams II. and III. compared with the tables of Part II. that the lines $L\gamma_4$, $L\beta_2$ and $L\gamma_1$, which according to the diagrams should fall out between xenon and krypton, were not observed for Rb and Sr.

§ 3. We will now proceed to a closer comparison of Bohr's theory of the development of groups of electrons in the atom with the experimental results as regards the first appearance of the lines in the X-ray spectra.

Starting from niton the lines which first disappear are β_5 and γ_6. For the elements in the neighbourhood of niton both the lines β_5 and γ_6 are fairly strong; in the neighbourhood of the Pt metals their intensity decreases very appreciably; for W, and especially for Ta, which elements both gave very good plates, they belong to the faintest known lines in the X-ray spectra. In the rare-earth metals and for Ba and Cs not the slightest trace of these lines has as yet been found. On several plates, however, I found white lines on a dark background in the place where we should expect to find β_5 or γ_6. As mentioned in II. § 9, these white lines are the characteristic absorption lines* L_1 and L_2 due to the absorption of the Cu radiation in the salts which were used upon the anticathode. Though even this is not an absolute proof† that the lines β_5 and γ_6 do not exist, it seems on the whole to be very probable that these lines disappear for the rare-earth metals. This is in agreement with the theory. According to this 5_3 orbits probably appear for the first time for La (57) ‡, but in the rare earths the electrons moving in these orbits are very loosely bound in the form of valency electrons, which are hardly present in the salts used in the experiments. It is only in Ta (73) and the following elements, that a 5_3 electron can first be expected to be present under the conditions of the experiments and to correspond to a binding sufficiently strong for the 5_3 level to be detected.

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* On carefully exposed photographs of an absorption edge usually a white line may be seen. This white line implies that the electron "prefers" the absorption of a frequency which is just able to bring it outside the atom.

† In studying the L_1 and L_2 absorption edges of tungsten, Duane and Patterson have also made use of the absorption in the tungsten of the anticathode. (See Proc. Nat. Ac. Sci. Washington, Sept. 1920.)

‡ Compare N. Bohr, *Zeitschr. f. Physik,* ix. p. 1 (1922).

We should expect the line $M\epsilon$ to disappear at the same time as the lines $L\beta_5$ and $L\gamma_6$, as the existence of this line is also bound to a 5_3 subgroup of electrons. This line has as yet not been studied systematically. It has been measured by Stenström * for U and Th and by Karcher † for the elements Bi, Au, and Pt.

§ 4. The appearance of the lines $M\alpha_1$, $M\alpha_2$, and $M\beta$ is connected with the existence of 4_4 electrons in the N-shell. According to Bohr, these electrons occur for the first time in the rare earths. For the elements Dy (66) there must already be electrons present in 4_4 orbits, as the appearance of the lines $M\alpha$ (α_1 and α_2 could not be separated for the elements with lower atomic number than Tl) and $M\beta$ has been established by Stenström for this element. The wave-lengths of these lines are respectively 9509 and 9313 X.U. It would be of interest to try to find these lines also for elements with lower atomic number than Dy.

§ 5 The existence of the line $L\gamma_4$ depends on the presence of 5_2 electrons in the O-shell. As pointed out to me by Professor Bohr, it appears from comparison with the optical spectra of Cd and In, that 5_2 orbits appear for the first time in the neutral atom of the latter element. The experimental results seem to indicate that for the line γ_4 there are certain complications. The very striking changes in the intensities of the pairs of lines β_5–γ_6 (see Part III. § 3) and β_2–γ_1 (see Part III. § 6) cannot be questioned. But usually it is very difficult to make any definite assertions concerning changes of the relative intensity of the lines with different elements, as we are not certain that they have been exposed under the same conditions. However, there is evidently a considerable change in the intensity of the line $L\gamma_4$ between the elements Sb and Sn. Down to In (49), this line could be measured but here it had become very faint. For Cd, where we according to Bohr should expect γ_4 to disappear, no certain information about this line could be obtained from the experiments. Extrapolating according to Moseley's law we find for the wave-length of γ_4 for Cd about 3081 X.U., which is at the same time about twice the wave-length of the copper $K\alpha_2$ line. Using an X-ray tube of brass and working with a fairly high tension which appeared to be necessary in photographing the very weak lines, it is impossible to avoid wholly the characteristic Cu-radiation. Actually the copper

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* Stenström, Dissertation, Lund, 1919.

† Karcher, Phys. Rev. II. xv. p. 285 (1920). The line $M\epsilon$ has been called $M\gamma_3$ by Karcher.

$K\alpha_1$ and $K\alpha_2$ lines though very faint were in second order observed on the plate. From a thorough examination of the plates, however, we are inclined to conclude that the line γ_4 does not exist for Cd or at any rate must be still weaker than in the case of In. For the next element (Ag) we are troubled by the increased absorption in the photographic plate (L_3 discontinuity), so that for this element nothing can be stated about the existence of γ_4. A complication showed in the photographs of the Pd (46) and Rh (45) spectra. Besides a very faint line at 3450 X.U. for Pd and at 3651 X.U. for Rh, which might be considered to be γ_4, another line of the same appearance was found for both elements. (For Pd $\lambda=3433$ and for Rh $\lambda=3631$.) These lines, however, have shorter wave-lengths than the extrapolated values of the respective L_3 discontinuities.

§ 6. The lines β_2 and γ_1 depend on the existence of the 4_3 electrons in the N-shell, which electrons according to Bohr are found for the first time in the neutral atom of Y (39). Relatively to the other lines of the L-spectrum β_2 and γ_1 have their ordinary intensity as far down as Mo. For Nb however they are considerably weaker compared with the other lines, for Zr they are both very faint. For Y, β_2 and γ_1 were not visible, but here the plates were not especially good. For Sr and Rb, for which the plates were quite good, γ_1 had wholly disappeared. If we extrapolate β_2 according to Moseley's law, this line almost coincides with β_4 in the case of Sr, while for Rb it should lie on the long-wave-length side of β_4. A faint line was actually found in this place. On different plates, however (taken with different Rb salts), the relative intensity of this line seemed to show considerable variations. This could easily be understood if the line were due to some other element. Thus it seems to be most probable that β_2 disappears at the same time as γ_1 between Zr (40) and Sr (38). The lines $M\gamma$ and $M\delta$ should disappear at the same time as $L\beta_2$ and $L\gamma_1$. As these lines must have a wave-length of about 37 A.U. for Nb, they cannot be studied in this region in the present state of spectroscopy.

§ 7. As for the line $L\beta_7$ it was not possible to identify it in the region under consideration. This line is also for the heaviest elements a rather faint line. For Pt and the elements with higher atomic number it seems to be a double line. This is difficult to explain in the light of our present knowledge of the X-ray spectrum. As has also been observed by Dauvillier, it is a single line for W, and I was able to observe the same thing for Ta. It will be very difficult to investigate β_7 in the region Ba–Rb, as it must coincide for several elements with β_{11} or β_{12} (see Part II. § 8). According to Bohr's theory we must expect that this line may perhaps occur as early as Rb, as for this element 5_1 electrons appear for the first time.

§ 8. It is a very important feature of Bohr's theory of atomic structure, that within the region of the rare-earth metals the N-shell is developed from a shell containing 3 subgroups of 6 electrons each with the quantum symbols 4_1, 4_2, 4_3, into a shell containing 4 subgroups of 8 electrons each with the quantum symbols 4_1, 4_2, 4_3, and 4_4 respectively. In favour of this view the following experimental facts may be considered. As is seen from the diagrams the energy difference between the N_3 level and the region outside the atom is given by the frequency difference of the $L\beta_2$ line and the L_1 discontinuity. This difference corresponds to a volt difference of 420 for Bi (83), 170 for W (74), 90 for Ba (56), and less than 10 for Ag (47). This means that in the region from Ba to W the binding of the 4_3 electrons increases much more slowly than in the regions from Ag to Ba and from W to Bi. This is just what we should expect from theoretical considerations. Within the region of the rare earths not only do the three subgroups of 4_1, 4_2, and 4_3 electrons increase by two electrons each, but also a new subgroup of eight 4_4 electrons is built up. As part of the orbits of the 4_3 electrons lies outside the orbits of the 4_4 electrons, and as a 4_3 electron during its revolution spends most of its time in this part where its velocity is smallest, the 4_4 electrons must be assumed to contribute appreciably to the total screening effect on the 4_3 electrons.

New measurements of the absorption discontinuities of the elements Ba–Sb which recently have been made by Mr. Lindsay in this laboratory give also a strong support to Bohr's theory. From the values of the L_3-discontinuities of these elements which Mr. Lindsay has kindly put at my disposal and my values of the wave-lengths of the line $L\gamma_4$ for the same elements, we are able to calculate the energy difference between the O_3-level and the outside of the atom. This difference, the value of which most probably corresponds to 30–40 volts for W (74), is still 30–25 volts for Ba (56) and Cs (55), but decreases to less than 10 volts for Te (52) and less than 6 volts for Sb (51). From this it appears very clearly that the outmost shells of the atom (O- and P-shell) do not change very much for the elements from W to Ba, but that these shells materially change for the elements with lower atomic number than Ba.

My researches in the L-series of the rare earths above quoted seem also to offer strong arguments in favour of Bohr's theory. The lines in the L-series, which are connected with N-levels, are: β_2, γ_1, γ_3, γ_2, β_6 and γ_5. Now for some of these lines remarkable anomalies of a new type were found. For both the lines β_2 and γ_1 rather faint satellites were observed at some distance on the long wave-length side *. Though we cannot yet account for this phenomenon, we should according to the theory expect some irregularities just in this region, accompanying the gradual transformation of the N-shell during the completion of the electronic configuration of 4-quantum orbits. For the lines γ_2 and γ_3 an analogous phenomenon was observed. As these lines lie very near to one another, it is somewhat difficult to interpret the photographs. The lines β_6 and γ_5 however, which are not very strong, seem to show no irregularities at all. More experimental data will soon be published.

§ 9. It is a fact well known to every one who has worked some time in X-ray spectroscopy, that on nearly every photograph taken of the X-ray spectrum of a single element there are found some lines which cannot be classified. It is probable that in most cases these lines are due to some other element, and very often this may actually be proved. The lines in the K-series of elements of higher atomic number, however, have not yet systematically been measured. If these lines appear in higher order on the plate, the identification will be impossible.

On the other hand, we must reckon with the possibility that some of the "unknown" lines really belong to the investigated element in question. In this case we must assume that the appearance of these non-systematic lines depends on special conditions, which are only fulfilled for one or very few elements. It appears from these considerations that conclusions which are based upon measurements of only one element have no great value for other elements.

There are several lines which cannot be inserted in such simple diagrams as I, II, and III, but which are found for

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* The other lines which cannot be inserted in a simple diagram lie always on the short wave-length side of a line with which they seem to be in some way connected.

several elements and can be classified according to Moseley's law. In the L-series these are the line β_8, which has been found on the short wave-length side of β_2 for a great number of the elements Ta-U *, and the lines which are dealt with in Part II. §§ 7 and 8 of this paper. In the K-series of the lighter elements similar lines have been found by Hjalmar †. Most of these non-diagram lines seem to disappear again for elements with higher atomic number. Another characteristic feature of these lines is that they always lie on the short wave-length side of a very strong diagram line with which they seem to be connected in some way ‡. Usually their frequency difference from this line is roughly proportional to the atomic number of the emitting element.

In order to explain the appearance of the non-diagram lines we might suppose that under certain conditions a sub-group of electrons from which one electron has been removed may give rise to more energy-levels than have been inserted in the diagrams. If this really is the case, these new levels must evidently play a different part from those which appear in the diagrams. As yet they have not been detected in the absorption spectra § : furthermore, they each seem to be connected with one line only and they usually disappear again for atoms of higher atomic number.

Again, part of these new levels might be attributed to a more complicated excitation of the atom. Suppose that when a high-speed β-particle collides with the atom, under certain conditions two electrons are removed at the same time. If then an electron were to fall back into the atom, this transition would give rise to a new line in the X-ray spectrum which would lie on the short wave-length side of a diagram line connected with the removal of only one electron. In this case we should expect to find a great difference between a characteristic X-ray spectrum excited by the impact of high-speed β-particles (primary radiation) and a spectrum excited by absorption of X-rays (secondary radiation). For the latter we should expect that no such non-diagram lines would appear. As some of these lines are quite strong,

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* *Zeitschrift f. Physik*, II. p. 191.

† *Zeitschrift f. Physik*, i. p. 439 (1920).

‡ The new lines recently detected for the rare-earth metals (see Part III. § 8) are an exception to this rule.

§ In this connexion it may be of interest to state that the structure found by Hertz (*Zeitschr. f. Phys.* iii. p. 19 (1920)) for the L_1- and L_2-discontinuities seems to be not directly connected with that which I have found for the L-α_1 and L-β_1 lines respectively.

we hope it may be possible to settle this question by experiment *.

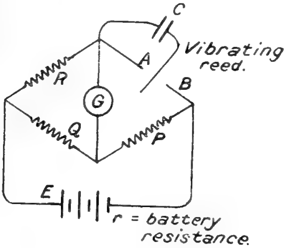
It gives me great pleasure to express my best thanks to Prof. M. Siegbahn of Lund and Prof. N. Bohr of Copenhagen, for the great interest they have shown in my work. I am also much indebted to my friend Mr. H. A. Kramers for his valuable help in reading the manuscript.

CXVI. *On a Development of Maxwell's Capacity Bridge.*

By V. A. Bailey, *M.A., The Queen's College, Oxford* †.

It is well known that one of the most accurate and convenient methods for determining Capacity in E.M. Units is that devised by Clerk Maxwell, shown in fig. 1.

Fig. 1.



One side of the condenser is made to touch A and B alternately n times per second by means of an electrically-driven tuning-fork or (as in the experiments of Thompson and Searle) by means of a rotating commutator. The galvanometer shows no deflexion when the following relation holds :—

$$nC = \frac{Q[(P+r)(Q+R+G)+Q(R+G)]}{[R(P+Q)+r(Q+R)][P(Q+R+G)+QG]},$$

P, Q, R, and r being the resistances of the conductors as indicated in the diagram, and C the capacity of the condenser.

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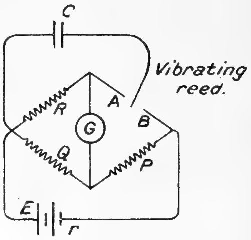
* (Note added during the proof.)—In this connexion attention may be called to a very interesting paper recently published by Mr. Wentzel (*Annalen der Physik,* lxvi. p. 937 (1921)). In this paper Mr. Wentzel clearly showed that most of the non-diagram lines arise in an atom which has lost more than one electron. I intend to deal in particular with the non-diagram lines of the L-series in another paper.

† Communicated by Prof. J. S. Townsend, F.R.S.

If the connexions be changed to the arrangement shown in fig. 2, the condition for no galvanometer deflexion is identical with that for Maxwell's arrangement.

Fig. 2.

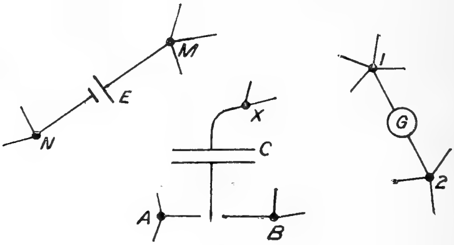


It is found, moreover, that the condition for no galvanometer deflexion is completely independent of the point in the network to which the condenser is permanently connected.

This is easily proved by the use of what may be termed the Principle of Superposition, namely: that in any network of conductors and sources of e.m.f., the current (or potential difference) between two junctions is equal to the algebraic sum of the currents (or potential differences) between the same two junctions produced by the e.m.fs. acting separately *.

We will, however, not do this for the arrangement shown in figs. 1 and 2, but will proceed straightway to examine the more general case of a network of conductors with r junctions (fig. 3).

Fig. 3.



Between junctions 1 and 2 there is a galvanometer, between junctions M and N a source of e.m.f. E, and a condenser of capacity C has one set of plates connected to junction X, while the other set of plates touch junctions A and B alternately n times a second.

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* This Principle can be shown to follow from the fact that all relations amongst the currents and e.m.fs. in a network are linear.

Let K denote the reciprocal of the resistance of a conductor (*i. e.*, its "conductance"), and let Δ_{pq} denote the minor of K_{pq} in the determinant

$$\Delta=\begin{vmatrix} K_{11} & K_{12} & \cdots\cdots & K_{1,r-1} \\ K_{21} & K_{22} & \cdots\cdots & K_{2,r-1} \\ \text{---} & \text{---} & \text{---} & \text{---} \\ K_{r-1,1} & K_{r-1,2} & \cdots\cdots & K_{r-1,r-1} \end{vmatrix},$$

taking K_{pp} as representing $-(K_{p1}+K_{p2}+K_{p3}+\ldots)$.

Let V_p, V_q, ... etc. denote the potentials at the points P, Q, ... etc., of any network, i_{pq} the current in PQ (from P to Q), and I_p, I_q, ... etc., the currents flowing *into the network* from outside.

In the particular case of E and all the I's vanishing except I_p and I_q (for which, of course, $I_p=-I_q$), it can be shown * that

$$i_{12}=\frac{K_{12}I_p}{\Delta}(\Delta_{2p}-\Delta_{2q}-\Delta_{1p}+\Delta_{1q}). \quad . \quad . \quad . \quad (1)$$

Similarly, if all the I's vanish, the effect of an internal e.m.f. E is given by relations of the form

$$V_a-V_b=\frac{K_{mn}E}{\Delta}(\Delta_{ma}-\Delta_{mb}-\Delta_{na}+\Delta_{nb}), \quad . \quad . \quad (2)$$

and

$$i_{12}=\frac{K_{12}K_{mn}E}{\Delta}(\Delta_{m1}-\Delta_{m2}-\Delta_{n1}+\Delta_{n2}). \quad . \quad (3)$$

These last two equations apply directly to the network of fig. 3, if the condenser is assumed to be out of action. To obtain the total effect in conductor 12 with C in action, we may calculate the total discharge per second through 12 due to C acting alone, and then superpose this on i_{12}.

When C touches A, the P.D. across it changes from V_b-V_x to V_a-V_x, i. e., by an amount V_a-V_b.

This causes a discharge $q=C(V_a-V_b)$ to pass through the network, in at X and out at A. Of this, q_1 say, will pass through 12. The ratio $\frac{q_1}{q}$ is plainly equal to the ratio of a current in 12 to the current I (in at X and out at A) which produces it. Hence, by equation (1),

$$\frac{q_1}{q}=\frac{K_{12}}{\Delta}(\Delta_{2x}-\Delta_{2a}-\Delta_{1x}+\Delta_{1a}).$$

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* *Cf.* Maxwell's 'Electricity and Magnetism,' 3rd edition, vol. i. chap. vi., or Jeans's 'Electricity and Magnetism,' chap. ix.

Similarly, when C touches B, a charge q_2 passes through 12, given by

$$-\frac{q_2}{q}=\frac{K_{12}}{\Delta}(\Delta_{2x}-\Delta_{2b}-\Delta_{1x}+\Delta_{1b}).$$

Hence, in one second the total charge passing through 12 is

$$n(q_1+q_2)=\frac{nK_{12}}{\Delta}(\Delta_{1a}-\Delta_{1b}-\Delta_{2a}+\Delta_{2b})C(V_a-V_b). \quad (4)$$

The absence of X from this expression shows that *the charge passing through* 12 *is independent of the point in the network to which the condenser is permanently attached.*

The galvanometer in 12 will give no deflexion when

$$i_{12}+n(q_1+q_2)=0,$$

i. e., by (2), (3), and (4), when

$$\frac{K_{12}K_{mn}E}{\Delta}(\Delta_{m1}-\Delta_{m2}-\Delta_{n1}+\Delta_{n2})$$
$$+\frac{K_{12}nC}{\Delta}(\Delta_{1a}-\Delta_{1b}-\Delta_{2a}+\Delta_{2b})$$
$$\times\frac{K_{mn}E}{\Delta}(\Delta_{ma}-\Delta_{mb}-\Delta_{na}+\Delta_{nb})=0.$$

This condition for balance reduces to

$$-nC=\frac{\Delta(\Delta_{m1}-\Delta_{m2}-\Delta_{n1}+\Delta_{n2})}{(\Delta_{1a}-\Delta_{1b}-\Delta_{2a}+\Delta_{2b})(\Delta_{ma}-\Delta_{mb}-\Delta_{na}+\Delta_{nb})}. \quad . \quad . \quad . \quad (5)$$

For the more general case of sources of e.m.f. in every branch of the network, the condition for no deflexion in the galvanometer can be shown in a similar way to be

$$-nC=\frac{\Delta}{(\Delta_{1a}-\Delta_{1b}-\Delta_{2a}+\Delta_{2b})}\cdot\frac{\Sigma[E_{mn}K_{mn}(\Delta_{m1}-\Delta_{m2}-\Delta_{n1}+\Delta_{n2})]}{\Sigma[E_{mn}K_{mn}(\Delta_{ma}-\Delta_{mb}-\Delta_{na}+\Delta_{nb})]}.$$

It is noticeable that the junction X does not appear either implicitly or explicitly in these last two equations, and hence we may draw the following interesting conclusion :—

In a general network like that shown in fig. **3** (*but also having several sources of e.m.f.*) *for which the variables have been adjusted so as to give no galvanometer deflexion, the permanently-connected plates of the condenser may then be connected to ANY point in the network without disturbing the galvanometer's state of no deflexion.*

This theorem evidently applies to the cases illustrated in figs. 1 and 2.

We can also show that this theorem may be extended to include inductances in the network.

For, by Ohm's law,

$$R_{pq}i_{pq} + L_{pq}\frac{di_{pq}}{dt} + \Sigma M_{rs}\frac{di_{rs}}{dt} = E_{pq} + V_p - V_q.$$

The initial and final values of i_{pq} and i_{rs} are the same. Hence, by integration :

$$R_{pq}q_{pq} = \int (E_{pq} + V_p - V_q)dt,$$

and similar equations for all the other pairs of junctions.

But this set of equations is identical with the set obtainable in the case of no inductance being present. Hence, inductances do not affect the distribution of the total charges, and neither, of course, do they affect the steady current distribution.

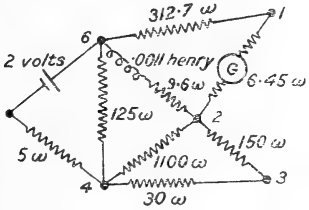
Experimental Verification.

The arrangement shown in figs. 1 and 2 was set up ($n=50$ per second, $C=1$ microfarad) and "balanced."

"Balance" was unaffected by connecting the condenser-terminal to a large number of points in the network taken in succession and at random. A difference of 1 in 5000 would have been noticeable if it had existed.

Another network examined was that shown in fig. 4.

Fig. 4.



A condenser of 4 microfarads made contact alternately on junctions 1 and 4 ($n=50$). The "balance" was found to be unaffected to less than 1 in 5000, as before.

My thanks are due to Prof. J. S. Townsend for his kind permission to carry out the experiments in the Electrical Laboratory, and also to Mr. R. I. Mincovitch for carrying out the arithmetical verification of formula (5) as applied to the last experiment.

Note.—Mr. H. F. Biggs has pointed out an extremely simple way of viewing the action of the condenser, which immediately leads to the conclusions already obtained. Since there can be no conduction-current in a perfect insulator, the total charge that passes into the network at the junction X during a complete period of the tuning-fork must be zero. The condenser-plates attached to the vibrating reed may be then regarded as conveying a charge $C(V_a - V_b)$ from A to B n times per second.

On this view, it immediately follows that the permanent connexion may be made with any part of the network without affecting the galvanometer "balance" when once made.

The Electrical Laboratory, Oxford.
June, 1921.

CXVII. *On the Selection Principle of the Quantum Theory.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

In a note titled "A Significant Exception to the Principle of Selection," and published in the April number of this magazine, P. D. Foote, F. L. Mohler, and W. F. Meggers describe some interesting experiments on the excitation of the lines of the arc spectrum of potassium, and conclude that the results of these experiments throw doubt on the general principles, on which the laws of the series spectra are interpreted on the basis of the quantum theory. As I shall try briefly to explain, the results in question do not seem, however, to offer sufficient basis for such a conclusion.

According to the ideas of the quantum theory each of the lines of a spectrum like the arc spectrum of potassium is emitted by the atom during a process of transition between two among a multitude of stationary states, in which one electron moves in an orbit, the dimensions of which are large compared with the orbits of the other electrons in the atom, which together with the nucleus may be said to form the inner system. In first approximation the orbit of the outer electron will be a plane central orbit, which may be described as a plane periodic orbit, on which is superposed a uniform rotation in its plane. In the stationary states of the outer electron the motion is therefore in first approximation fixed in the well-known way by means of two quantum numbers, which may be denoted by n_1 and n_2. While n_1

refers to a certain condition concerning the radial motion of the electron, n_2 fixes the angular momentum of the electron round the centre of the orbit through the condition that this angular momentum is equal to $n_2h/2\pi$. These numbers are assumed to be related to the spectral terms in such a way that n_1 increases by one unit when, within each series of terms, we proceed from one member to the next, while n_2 remains constant within each series of terms and increases by one unit when we pass from the S-terms to the P-terms, and from the P-terms to the D-terms, and so on. This classification of the terms refers, however, only to the structure of the arc spectra in large features. In order to account for the complex structure of the lines (doublets, triplets) a higher degree of complexity of the multitude of stationary states is claimed. This is assumed to arise from a complication of the motion of the outer electron due to a small departure from central symmetry of the inner system, which causes the plane of the orbit of the outer electron to undergo a slow precession round an axis coinciding with the axis of angular momentum of the atom. Due to this complication of the motion there will in the fixation of the stationary states appear a third quantum number n_3, which fixes the orientation of the plane of the outer electron relative to the axis of the inner system through the condition that the resultant angular momentum of the atom is equal to $n_3h/2\pi$. This third quantum number is related to the complexity of the multitude of spectral terms in such a way that the components of a set of complex terms corresponding to the same values of n_1 and n_2 are distinguished by different values of n_3.

Now the so-called principle of selection originates from considerations dealing with the limitation of the possibility of transition between stationary states. Such considerations are based on two entirely different types of arguments. One argument rests upon the so-called *principle of correspondence* according to which the possibility of a transition between two stationary states, giving rise to the emission of a train of harmonic waves, is sought in the presence in the motion of the atom of a certain "corresponding" constituent harmonic vibration. For stationary states of the atom of the type described above, this argument leads to the conclusion that, at the same time as no limitation is imposed on the variation of the quantum number n_1, the number n_2 must by a transition always change by one unit, while the number n_3 may either change by one unit or remain unchanged. Another argument is obtained from the fact that it is possible in certain cases to exclude transitions between stationary states from the condition of *conservation of angular momentum* during the radiation process. As regards the problem under consideration this leads to the conclusion, that the quantum number n_3, which, as mentioned, is directly related to the resultant angular momentum of the atom, by a transition cannot vary by more than one unit, while no direct information as regards a limitation of the quantum numbers n_1 and n_2 can be obtained from this argument.

As regards the comparison of these conclusions with experiments, our insight into the origin of the complex structure of spectral lines is at present hardly sufficiently developed to provide a definite test as regards the detailed interpretation of the quantum number n_3 and therefore of the rules of selection as far as they can be based entirely on considerations of conservation of angular momentum. At present the main problem, with which also the experiments in the above-mentioned note deal, is the test of the conclusions as regards the variation of the quantum numbers n_1 and n_2, on which in first approximation the spectral terms depend. Now previous experimental evidence as regards excitation of series spectra has seemed convincingly to support the conclusion drawn from the principle of correspondence, that under circumstances where the emitting atoms are not influenced by external agencies, only such spectral lines can appear as correspond to a combination of terms for which n_2 differs by one unit. This may be considered as a very important result, because we may say that the quantum theory, which for the first time has offered a simple interpretation of the fundamental principle of combination of spectral lines, at the same time has so to say removed the mystery which has hitherto adhered to the application of this principle on account of the apparent capriciousness of the appearance of predicted combination lines. Especially attention may be drawn to the simple interpretation which the quantum theory offers of the appearance observed by Stark and his collaborators of certain new series of lines, which do not appear under ordinary circumstances, but which are excited when the emitting atoms are subject to intense external electric fields. In fact, on the correspondence principle this is immediately explained from an examination of the perturbations in the motion of the outer electron, which give rise to the appearance in this motion—besides the vibration already present in a simple central orbit—of a number of constituent harmonic vibrations of new type and of amplitudes proportional to the intensity of the external forces. To call such an effect, as is often done, a "breaking through" of the principle of selection is a terminology which would not seem to be quite adequate in view of the character of the theoretical interpretation which can be given of the phenomenon under consideration.

In the new experiments published in the note, mentioned in the beginning of this letter, precautions were taken to screen the radiating atoms from the effect of external electric forces due to the potential applied to the discharge tube. In spite of these precautions it was found that under certain conditions the spectra observed included, besides the usual arc lines of potassium, certain lines corresponding to combinations between two terms, for which n_2 differs by two units, and which correspond to the new series mentioned above, which appear when the radiating atoms are exposed to intense electric fields. This observation is by the authors described as a significant exception to the principle of selection, since the appearance of the lines could evidently not be caused by external fields of the same type as claimed for the production of the ordinary Stark effect. From a closer consideration of the experimental conditions it would appear, however, that the observations published rather support than disprove the theory. First of all it was found that the lines in question appeared only if very dense currents were sent through the apparatus, while these lines did not appear when a discharge of less current density was passed through the tube. Thus under the circumstances, where the condition of non-disturbance of the atoms by external agencies, claimed by the theory, was satisfied to the highest degree, no exception from the simple selection rule was observed, indicating that the presence of the new lines for higher current densities was caused by some agency influencing the usual motion of the electrons in the atoms. Looking for some such effect, it would appear that, just due to the screening from external forces, the experimental arrangement described would be especially favourable for the accumulation of ions in the region of the discharge tube used for the observation of the spectrum; an effect to which already the authors themselves incidentally refer as a possible cause of the origin of the new lines. Without closer information about the dimensions of the apparatus and the details of construction than that given in the note, it is not possible to form an accurate estimate of the density of ions which may have been present under the conditions of the experiments; but already a rough calculation makes it very probable that the fields, due to neighbouring ions and free electrons, to which the emitting atoms have been subject, have been of the order of magnitude claimed by the quantum theory for the appearance of the new lines with the intensity observed. Especially it must be noted, that the intensity of these fields may easily have been many thousand times larger than the intensity of the external electric forces present in the unscreened part of the apparatus, as a direct consequence of the applied potential.

On the whole it seems that the theory of series spectra based on the quantum theory allows to account in a general way for the experimental evidence, and that especially the relative intensity, with which under various experimental conditions combination lines appear, may not be considered as presenting the theory with serious difficulties, but rather as providing a means of investigating the conditions under which spectra are emitted. For instance, investigations of the presence of combination lines may perhaps offer the most direct means of estimating the density of ions in the different parts of a discharge tube. As regards a more detailed account of the theory of series spectra, and for references to the literature on this subject, the reader of this Magazine may be referred to a paper on the effect of electric and magnetic fields on spectral lines, which was read by the writer as a Guthrie lecture at the Physical Society of London on March 24th, and which will soon appear in the Proceedings of this Society.

Yours faithfully,
N. Bohr.

University, Copenhagen,
April 11th, 1922.

CXVIII. *X-ray Electrons.* *By* R. Whiddington, *M.A., D.Sc., Cavendish Professor of Physics, University of Leeds*[*].

[Plate XXIV.]

Introduction.

It has been known for many years that X-rays have the power of ejecting high-speed electrons from the surface of materials on which they are incident.

The earliest successful attempts to measure the speed of these X-ray electrons were made by Dorn in 1900 and

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[*] Communicated by the Author.

Innes in 1907, and it appeared from their results that the speed lay between 6 and 8×10^9 cm./sec. and was independent of the intensity of the X-rays.

In 1912 the writer attacked the problem from a different angle by interpreting the absorption experiments of Beatty* in the light of the fourth-power law of velocity diminution previously established †.

Beatty having measured the range in air of X-ray electrons, it was possible to translate the range into terms of initial speed, and it was shown that this ejection speed was nearly equal to $10^8 \times A$, where A is the atomic weight of the element supplying the X-rays †.

It was pointed out recently that this result—frankly approximate in view of the nature of the experiments—was expressible in terms of atomic number, and that for these fastest X-ray electrons a formula similar to that of Moseley for X-rays was approximately true ‡.

It is to be noted, however, that the method just mentioned is only capable of determining, approximately, the speed of the fastest electrons, and is incapable of proving with certainty the existence of independent groups of smaller speed—unless, of course, such groups are very widely separated §.

The present work was undertaken with the object of extending these results, and during its progress de Broglie ‖ has published most important results bearing on the same problem. His results, which will be referred to in more detail later, are confirmed in the main by my own observations.

The Apparatus.

The apparatus used to determine the speed of the X-ray electrons is indicated in fig. 1 ¶.

A quartz bulb B is fitted with cathode C and rhodium-faced target T, water-cooled through the tubes D_1, D_2.

The cathode also was air-cooled by the copper radiator fins R.

Just under T and about a centimetre above it is mounted the aluminium slit chamber J (shown enlarged to the right),

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* Beatty, Proc. Roy. Soc. (1910).

† Whiddington, Proc. Roy. Soc. (1912).

‡ Whiddington, Phil. Mag. vol. xxxix. p. 694 (1920).

§ Simons, Phil. Mag. (1921), has repeated Beatty's experiments very carefully, and has shown the existence of such groups.

‖ de Broglie, *Comptes Rendus* (1921).

¶ A preliminary account was given in Proc. Camb. Phil. Soc. (1921).

on the three inside faces of which the element providing the X-ray electrons was spread in the form of thin metal sheet or powder.

The upper side of J was a sheet of aluminium thin enough to transmit the X-rays from T with small absorption, but thick enough to absorb completely any direct electrons produced within B[*].

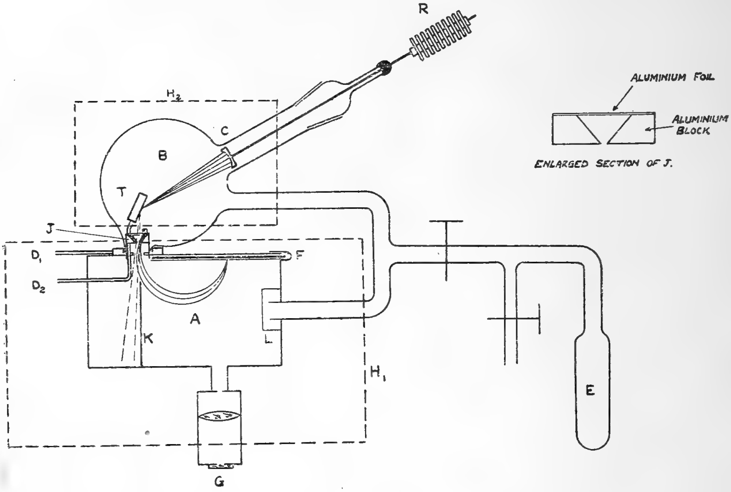

Fig. 1.

A is the camera chamber, made on the plan adopted by Rutherford and Robinson[†] in their β-ray speed measurements, so that, with a uniform magnetic field applied at right angles to the plane of the figure, the electrons from J came to a focus on the photographic film F.

The slit was ·05 cm. in width.

K is a thick brass partition stretching right across the camera so as to prevent any secondary radiation from the inside of the camera from reaching F.

L is a light trap to minimize the effect on F of any stray light from outside or from accidental discharge passing down the glass evacuating tubes.

G is a collimator for projecting a registration spot of light on F whenever necessary.

The usual pump and liquid-air charcoal tube method of evacuation was adopted.

The discharge was produced with an ordinary induction

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[*] This necessary thickness d is calculable from $d=v^4/a$ given in Proc. Roy. Soc. (1912).

[†] Phil. Mag. vol. xxvi. p. 717 (1913).

coil and mercury break, with an auxiliary mechanical rectifier. A maximum input of 1000 watts was used.

The magnetic field was provided by two large air-core coils (H_1) placed such a distance apart as to produce a sensibly uniform field over the area of the camera. Auxiliary small coils H_2 in series with H_1 were so arranged as to compensate the external field of H_1 over the path traversed by the cathode rays between C and T.

The uniformity and value of the field was investigated by search coil and ballistic galvanometer in the usual way. A current of 7 amperes in the coils gave a uniform magnetic field of 101·4 Gauss*.

It is clearly an advantage in this kind of work to use air- rather than iron-cored wires, since

(1) The value of the field is always directly proportional to the current traversing the coils, and it is therefore easy to adjust the field to any required value without troublesome remeasurement.

(2) A small accidental variation of current produces only a proportionate change in the field.

(3) The compensating coil having been set for any one value of the field is set also for any other value.

The disadvantage is that rather large electrical energy is consumed by the field coils—in the present case, about 500 watts.

The radii of curvature of the electrons varied from about 3 to 6 cms.

Taken as a whole, the apparatus just described is very troublesome to manage owing to the difficulty of keeping the numerous metal, quartz-glass joints air-tight. In spite of water-cooling, the joints too frequently give way. Its main recommendation is on the ground of economy, since the expensive Coolidge tube and alternator transformer is not required on account of the high efficiency of the arrangement.

This efficiency is obtained

(1) Because the X-ray electrons are liberated from three surfaces within J.

(2) Because the target T being very near J, the intensity of the X-rays is very great.

The second reason just given is particularly important. An ordinary X-ray bulb could not easily be arranged nearer than say 10 cms. to J, with a consequent 100-fold loss of intensity.

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* Since H_2 is small compared with H_1, one would expect its external field to be negligible in H_1. This was proved by showing that the value of RH was constant for some definite speed group of electrons and thus independent of the actual path traversed in H_1.

Method of taking Photographs.

The film used was the Duplitized X-ray film of Messrs. Kodak. A faint impression could be obtained with 5 minutes' exposure from a copper foil, and a good photograph in 30 minutes.

It was observed that the intensity of the photographs obtained was not proportionately increased by longer exposure, while at the same time the contrast became less pronounced. Without further discussion, it may be of interest to mention that excellent results were sometimes obtained from these duplitized films by dividing the exposure into two parts, one on each side of the film. It was necessary, of course, to ensure that the film was placed in exactly the same position relative to the camera during each exposure, and this could be tested by the collimator G of fig. 1. The lower photograph in Pl. XXIV. was obtained by this means.

In order to test the resolving power, so to speak, of the apparatus the chamber J was removed, the apparatus exhausted with film in place, and a discharge passed from an electrostatic influence machine working with no condenser. Under these conditions the cathode rays were reflected from T through the slit into A and then bent round to foci on F. The discharge was intermittent, so that a velocity spectrum was produced giving the result shown in the top reproduction in the Plate. It is clear that the focussing is excellent, and that the individual lines are sharply defined and practically as narrow as the original slit *.

The fundamental product ρH was measured from the photographs obtained with an accuracy, it is believed, of $\frac{1}{2}$ per cent. It is to this accuracy, then, that the velocity of the electrons corresponding to an intense well-marked line can be guaranteed.

Since, however, it is convenient to express the results in terms of energy rather than velocity, it is proposed to define an electron in "equivalent frequency" ν, defined by the usual relation $h\nu=\frac{1}{2}mv^2$, the relativity correction having been introduced in calculating v from $\rho\mathrm{H}=v\,.\,m/e$.

It is clear, therefore, that ν will be subject to a possible

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* Neglecting the relativity correction, $\frac{d\rho}{dv}=\frac{1}{\mathrm{H}}\,.\,m/e$, where ρ is the radius of curvature of an electron velocity v in field H. It can easily be shown from this that the "dispersion" and "resolving power" for the apparatus is nearly independent of v—or the spectrum is normal for a given value of H.

error of 1 per cent.—an error which is likely to be even greater in the case of faint lines presenting difficulty in measurement.

Experimental Results.

Eight elements have so far been examined for X-ray electrons under the action of the radiation from Rhodium [45], viz.: Aluminium [13], Copper [29], Zinc [30], Arsenic [33], Strontium [38], Molybdenum [42], Tungsten [74], Bismuth [83].

One typical photograph is shown (lower of Pl. XXIV.) of copper.

As noted by de Broglie, there are a number of lines or rather bands coming to a more or less sharply-defined head on the high-velocity side. To each band de Broglie attaches a maximum v and therefore ν corresponding to the ρH value of the head *. This maximum value, in fact, is associated with electrons escaping from the surface atoms of the material with a speed unaffected by subsequent passage through or near other atoms: it may, in fact, be taken to be the value corresponding to emission from a free atom.

It is these maximum values of ν which have been tabulated below.

TABLE.

	ν.	Origin of electron.	Agency of ejection.	ν expected from origin and agency.
		COPPER (metal leaf).		
s.	172	L Ring	CuK_α	$\mathrm{CuK}_\alpha-\mathrm{CuL}=173$
s.	193	L Ring or outer rings or free	CuK_β or CuK_α	$\mathrm{CuK}_\beta-\mathrm{CuL}=194$ $\mathrm{CuK}_\alpha=195$
f.	217	outer rings or free	CuK_β	$\mathrm{CuK}_\beta=216$
s.	270	K Ring	RhK_α	$\mathrm{RhK}_\alpha-\mathrm{CuK}=273$
f.	287	?	?	
s.	313	? K Ring	RhK_β	$\mathrm{RhK}_\beta-\mathrm{CuK}=334$
s.	461	L Ring	RhK_α	$\mathrm{RhK}_\alpha-\mathrm{CuL}=468$
f.	502	L Ring outer or free	RhK_β RhK_α	$\mathrm{RhK}_\beta-\mathrm{CuL}=529$ $\mathrm{RhK}_\alpha=490$
v.f.	552	outer or free	RhK_β	$\mathrm{Rh}_\beta=551$

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* I have applied an obviously necessary correction in measurement instead of ρH. I use $[\rho-\delta/4]$H where δ=slit width.

	ν.	Origin of electron.	Agency of ejection.	ν expected from origin and agency.
		ZINC (oxide).		
s.	189	L Ring	ZnK_α	$ZnK_\alpha - ZnL = 185$
s.	215	L Ring outer or free	ZnK_β ZnK_α	$ZnK_\beta - ZnL = 208$ $ZnK_\alpha = 209$
f.	234	outer or free	ZnK_β	$ZnK_\beta = 232$
s.	260	K Ring	RhK_α	$RhK_\alpha - ZnK = 267$
f.	280	?		
s.	318	? K Ring	RhK_β	$RhK_\beta - ZnK = 328$
s.	456	L Ring	RhK_α	$RhK_\alpha - ZnL = 466$
		Other bands too nebulous to measure of higher frequency.		
		ALUMINIUM (metal).		
f.	448	K Ring	RhK_α	$RhK_\alpha - AlK = 452$
v.f.	502	K Ring	RhK_β	$RhK_\beta - AlK = 513$
		ARSENIC (oxide).		
	222	L Ring	AsK_α	$AsK_\alpha - AsL = 221$
s.	251	L Ring outer or free	AsK_β AsK_α	$AsK_\beta - AsL = 250$; $AsK_\alpha = 252$
f.	270	outer or free	AsK_β	$AsK_\beta = 285$
s.	442	L Ring	RhK_α	$RhK_\alpha - AsL = 455$
f.	507	L Ring outer or free	RhK_β RhK_α	$RhK_\beta - AsL = 516$ $RhK_\alpha = 490$
v.f.	563	outer or free	RhK_β	$RhK_\beta = 551$
		STRONTIUM (oxide).		
s.	292	L Ring	SrK_α	$SrK_\alpha - SrL = 296$
s.	334	L Ring outer or free	SrK_β SrK_α	$SrK_\beta - SrL = 337$ $SrK_\alpha = 335$
v.f.	370	outer or free	SrK_β	$Sr_\beta = 385$
s.	426	L Ring	RhK_α	$RhK_\alpha - SrL = 442$
f.	412	L Ring outer or free	RhK_β RhK_α	$RhK_\beta - L = 503$ $RhK_\alpha = 490$
f.	544	outer or free	RhK_β	$RhK_\beta = 551$

	ν.	Origin of electron.	Agency of ejection.	ν expected from origin and agency.
		MOLYBDENUM (oxide).		
s.	361	L Ring	MoK_α	$MoK_\alpha - SrL = 364$
s.	491	L Ring outer or free	MoK_β MoK_α	$MoK_\beta - SrL = 416$ $MoK_\alpha = 424$
v.f.	475	outer or free	MoK_β	$MoK_\beta = 476$
		TUNGSTEN (oxide).		
s.	164	M Ring	WL_α	$WL_\alpha - WM = 162$
s.	203	M Ring outer or free	WL_β WL_α	$WL_\beta - WM = 202$ $WL_\alpha = 202$
s.	241	M Ring outer or free	WL_γ WL_β	$WL_\gamma - WM = 242$ $WL_\beta = 242$
v.f.	277	outer or free	WL_γ	$WL_\gamma = 282$
f.	330	?		
s.	445	M Ring	RhK_α	$RhK_\alpha - M = 450$
f.	494	outer or free	RhK_α	$RhK_\alpha = 490$
v.f.	544	outer or free	RhK_β	$RhK_\beta = 551$
		(Much general fog.)		
		BISMUTH (oxide).		
	207	M Ring	WL_α	$BiL_\alpha - BiM = 204$
	260	M Ring outer or free	WL_β WL_α	$BiL_\beta - BiM = 260$ $BiL_\alpha = 260$
	312	M Ring outer or free	WL_γ WL_β	$BiL_\gamma - BiM = 316$ $BiL_\beta = 316$
f.	368	outer or free	WL_γ	$BiL_\gamma = 372$
f.	479	N Ring outer or free	RhK_α	$RhK_\alpha - BiN = 484$ $RhK_\alpha = 490$
f.	538	N Ring outer or free	RhK_β	$RhK_\beta - BiN = 545$ $RhK_\beta = 551$
		(Much general fog.)		

The explanation of most of the bands observed is possible by applying the energy-difference relations suggested by Rutherford in 1914 for the β-rays and applied by de Broglie to his experiments. There are some lines, however, which are somewhat ambiguous. It will be assumed that the rhodium target emits—in addition to "white" radiation—a very strong monochromatic radiation RhKα [$\nu = 490 \times 10^{16}$], together with a much feebler frequency RhK$_\beta$ [$\nu = 551 \times 10^{16}$].

If the radiations characteristic of the element under consideration are excited, it will be necessary to take into account also the radiation frequencies K_α, K_β ... in the K series and L_α, L_β ... in the L series, M_α, M_β ... in the M series, etc., and also the corresponding absorption-limit frequencies K, L, M ... in the following manner :—

The X-ray electrons—*i. e.* the electrons liberated by the X radiation—will have energies corresponding to their origin. Electrons liberated from the more deep-seated rings nearer the nucleus will have less energy than those liberated from the outer rings.

Thus the Rhα radiation may liberate electrons with energies proportional to the frequency differences :

RhKα − K (electron from K ring),
RhKα − L (electron from L ring),
RhKα − M (electron from M ring),
etc., etc. ;

and if it be possible for the free electrons to absorb the X-ray energy :

RhKα (free electron).

There may also be a much smaller liberation of electrons corresponding to :

RhK$_\rho$ − K,
RhK$_\rho$ − L,
RhK$_\rho$ − M,
. . . . . .
RhK$_\rho$,

producing much fainter impressions in the photographs.

In addition to these sets of electrons, there may be other sets liberated by the K, L, etc. X radiations excited in the element under examination.

The K_α line cannot liberate an electron from the K ring, since its energy is not sufficient; but there may be

$K_\alpha - L$ (from L ring) $K_\beta - L$,
$K_\alpha - M$ (from M ring) $K_\beta - M$,
. . . .
K_α (free electron ?) K_β ;

and similarly for the L radiation, although in this case the spectrum is somewhat more complicated by the presence of a comparatively strong L_γ radiation.

In the table are shown the equivalent frequencies of the X-ray electrons for the eight elements examined.

In the second column is indicated the position within the atom from which the electron may be supposed to come; while the third column shows by what agency the ejection is effected.

The fourth column gives the value of ν to be expected from the suggestions of columns 2 and 3.

Discussion of Results.

I. Broadly speaking, there is a general agreement between the observed and calculated values of the effective frequencies (ν) for these X-ray electrons.

Taking copper for example: The three lines of smallest frequency are to be ascribed to the action of K_α and K_β of copper on the rings outside the K ring, and it is to be noted that the central line of the triplet is to be regarded as due to two sets of electrons—one from the L ring, the other from the outer rings or even from free electrons. Further, the line 217 ascribed to the ejection from the outer rings (or possibly the lifting out of free electrons) * is very faint—an observation in agreement with Rutherford and Ellis's β-ray results.

This characteristic K triplet is repeated in the case of zinc, arsenic, strontium, and molybdenum. In the case of tungsten and bismuth, however, the K radiation is not excited, and in place of the K triplet we get the L quadruplet, the additional line being due to the presence of three strong lines L_α, L_β, and L_γ in the L X-ray spectrum.

At the other end of the copper electron spectrum are two lines, 502 and 552, very faint and probably due to RhK_α and RhK_β, ejecting electrons from the outer rings or lifting free electrons from the surface of the material as a whole. The apparatus, of course, is not capable of differentiating between these two possibilities.

Of the four remaining lines, 270 is clearly due to a K-ring electron ejected by the RhK_α radiation, while 461 is an L-ring electron ejected by the RhK_β radiation.

The remaining two lines are rather puzzling. 287 is a faint line, and may therefore be inaccurately measured, but 313 is a strong well-defined line. The nearest straightforward interpretation is to place it as a K-ring electron ejected by RhK_β, in which case the expectation for ν would be 334. This is a far bigger difference than is to be expected

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* See Millikan, Phys. Rev. 1921, p. 243.

for so bold a line; moreover, its intensity is greater than the RhK_β radiation should give *.

II. A point which is not brought out in the table and which should be mentioned is that the electron emission increases as the atomic number increases. In fact, the time of exposure necessary to produce a photograph of a certain intensity is very roughly inversely proportional to the atomic number. With the elements of higher atomic number, also, there is a very considerable amount of continuous spectrum, due possibly to the preponderating importance of X-ray electrons ejected by the "white" radiation from the target.

III. It is clear from reference to the copper X-ray electron spectrum that, although each line shows a more or less sharply-defined head or boundary on the high-velocity side, yet there is in addition more than a suggestion of breadth. Measured in terms of equivalent frequency, this breadth is explicable on the supposition that these lines are really doublets, unresolved by the apparatus and separated approximately by frequency M.

IV. It is to be noticed finally that whenever a frequency difference less than that corresponding to the K (or L as the case may be) might have been expected, no corresponding line is observed. Thus, in the arsenic spectrum $RhK_\alpha - AsK = 202$, which is less than $AsK = 288$, and no line appears at 202; or, again, in the bismuth spectrum $RhK_\alpha - BiL = 91$, which is less than $BiL = 399$, and no line appears at 91.

Further, although the L electron lines are strong in the cases of tungsten and bismuth when the K electrons are not disturbed, yet in other cases—copper, for example—no trace of L electrons could be found, although a careful search for them was made.

Experiments are being continued.

My thanks are due to the Government Grant Committee of the Royal Society for assistance in defraying the cost of the quartz apparatus.

The University of Leeds,
April 3rd, 1922.

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* Zinc impurity in the copper-leaf would reduce the discrepancy somewhat, but hardly sufficiently. Whatever the explanation—and further experiment is in progress—it may be pointed out that the triplet (270, 287, 313) is complementary member for member with (217, 193, 172), in the sense that when corresponding members are added together the total approximates closely to 490 (RhK_α).

CXIX. *The abnormally long Free Paths of Electrons in Argon. By* J. S. Townsend, *M.A., F.R.S., Wykeham Professor of Physics, Oxford, and* V. A. Bailey, *M.A., Queen's College, Oxford* *.

In the March number of the Philosophical Magazine we gave the results of experiments on the motion of electrons in pure argon which showed that the mean free path of the electrons is much greater in argon than in nitrogen or hydrogen, and that the loss of energy of an electron due to a collision is much less in argon than in these two gases, for velocities of agitation of the electrons between $8\cdot5\times10^7$ and 14×10^7 cm. per second.

Within this range of velocities the free path in argon increases as the velocity of agitation diminishes, and it is of interest to find whether the free path continues to increase when further reductions are made in the velocity.

With the same electric force and gas pressure the velocity of agitation of the electrons is much higher in argon than in the other gases, and it would be necessary to prepare a very large quantity of pure argon or to use extremely small electric forces in order to obtain small velocities of agitation in the pure gas. It is undesirable, for experimental reasons, to adopt either of these methods.

The velocity of agitation may, however, be reduced to very low values by adding hydrogen to the argon, and the mean free paths of the electrons may be found for the mixture by determining the velocity in the direction of the electric force and the velocity of agitation, by the method we have already described. The mean free path in argon may thus be found in terms of the mean free path in hydrogen.

Experiments on this principle were made with an improved apparatus which was first carefully tested with pure hydrogen admitted through a palladium tube. The velocities in hydrogen which were obtained, agreed with those already given within experimental errors which may be taken as not exceeding 3 per cent.

The results of some experiments with the mixture are given in the following table, Z being the electric force in volts per centimetre, W_h the velocity in cms. per second in the direction of the electric force, u_h the velocity of agitation of electrons in pure hydrogen at 5·1 millimetres pressure, W_m and u_m the corresponding velocities with the same electric force in the mixture consisting of hydrogen

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* Communicated by the Authors.

at 5·1 millimetres pressure and argon at 20 millimetres pressure.

Z.	$W_h \times 10^{-5}$.	$W_m \times 10^{-5}$.	$u_h \times 10^{-7}$.	$u_m \times 10^{-7}$.
17	21	19·1	5·15	5·3
8·5	15·1	14	4·1	4·2
4·1	10·9	10·2	3·2	3·1

The addition of the argon to the hydrogen does not reduce the velocity of agitation, under these conditions, by an appreciable amount, as the figures in the last two columns are the same within the limits of experimental errors. The proportion in which the velocity in the direction of the electric force is reduced, by adding the argon to the hydrogen, is small, and diminishes with the force.

Since the velocities u are not appreciably different in the pure hydrogen and in the mixture, the ratio of the mean free path l_h in the hydrogen to the mean free path l_m in the mixture is $l_h/l_m = W_h/W_m$. The mean free path l_a in argon at 20 millimetres pressure in terms of l_h is obtained from the relation $1/l_m = 1/l_h + 1/l_a$.

Taking the results of the experiments with a force of 8·5 volts per centimetre it is seen that, with a velocity of agitation of $4{\cdot}2 \times 10^7$ cm. per second, the mean free path in argon is about 60 times the mean free path in hydrogen at the same pressure.

For this velocity the mean free path, previously obtained, in hydrogen at one millimetre pressure is 0·26 millimetre, so that the mean free path in argon at one millimetre pressure is about 15 millimetres, or fifty times the mean free path deduced from the atomic radius which is obtained from the viscosity.

The experiments show that the reduction of the velocity W in hydrogen by adding argon having four times the pressure of the hydrogen, is too small to permit of an accurate determination of the mean free path in argon.

We intend to make further experiments on this principle using mixtures in which the pressure of the hydrogen is about 5 per cent. of that of the argon, and to determine the free paths for velocities of agitation much below $4{\cdot}2 \times 10^7$ cm. per second.

CXX. *Viscosity of Air in a Transverse Electric Field.* By Satyendra Ray, *M.Sc. Allahabad University, Research Student, University College, London* *.

QUINCKE† found a change in the viscosity of liquids in an electric field. Spheres of crown and flint glass &c. 1 cm. in diameter were suspended by fine silk fibres attached to the arms of a balance. The logarithmic decrement was observed with and without a field due to 2000 volts, the distance between the plates being 1·5 cm. The difference, which he calls electric viscosity, was 0·0398 in the case of a crown glass sphere in liquid ether when the force was transverse to the motion. Parallel to the lines of force the viscosity also increases but to a smaller extent.

Again in the case of gases the Faraday Mosotti theory of dielectrics is very well satisfied as has been tested by Boltzmann ; and if polarization physically means an orientation of molecules or a kind of tidal distortion of the molecule, a change in the effective area of the cross section and a consequent change in the viscosity with the electric field might be expected.

To test whether there is any change in the case of gases the transpiration method was employed. The usual capillary tube was replaced by two steel plates 2 feet long, 2 inches broad, and 1 inch thick. One face of each was planed and these plane faces were placed parallel to and facing each other. The plates were separated from each other by three bits of drawn glass thread nearly 1 cm. long on which the top plate was laid as on rollers. The sides were painted with molten resin and wax, this method being found the best to make the tube simultaneously electrically as well as pneumatically tight. The tube thus formed by parallel plates with lateral walls was connected with the usual Mariotte's bottle arrangement by means of a tin box fitted on one end of the tube with wax and resin. Paraffin oil was used in the Mariotte's bottle in the first instance, and the time of transpiration of a definite volume under constant pressure was noted with and without the electric field. Latterly, however, to eliminate complications arising from the use of paraffin oil, dry air was sucked through instead. For this purpose a second box was attached to the other end of the tube and connected up with a sulphuric acid wash-bottle through which the air was drawn in. The time for running out

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* Communicated by Prof. A. W. Porter, F.R.S.

† Quincke, *Ann. d. Phys. u. Chem.* lxii. (1897).

water between two marks on the aspirator gauge (and afterwards for running out a definite volume of water, equal to 800 c.c. nearly), starting from the same initial conditions, was taken with and without the field.

Assuming the motion to be non-turbulent, which we reasonably can do, the viscosity must vary directly as the time of outflow. In the experiment a potential difference of 580 volts between plates ·31 mm. apart did not produce a change of even 1 sec. in 9 min. 39 sec. The potential gradient was 18000 volts per cm. nearly, the sparking potential gradient being 31000 volts per cm.

In setting an upper limit to a possible change in the viscosity due to the electric field, attention must be paid to the "resistance" of the other parts of the channel besides the tube. The time of flow without the field was to the time of flow with it as 4·5 : 10 nearly. The resistance of the tube may therefore be taken to be (10 − 4·5)/10 of the total resistance. The present experiment may therefore be interpreted to prove the absence of any change in the viscosity of air greater than or equal in amount to ·3 per cent.

I am grateful to Prof. A. W. Porter for his kind interest in the experiment and for his valuable suggestions.

1st May, 1922.

CXXI. *Notices respecting New Books.*

Multilinear Functions of Direction and their uses in differential geometry. By E. H. Neville, late Fellow of Trinity College, Cambridge, Professor of Mathematics in University College, Reading. (Cambridge: At the University Press. 8*s.* 6*d.* net. 1921.)

In this small book Prof. Neville has given a systematic discussion of functions of several independent directions. In the course of the development of ideas which are to some extent generalizations of the ideas of differential geometry, a number of propositions which actually occur in modern differential geometry are included. The way in which these theorems are involved in the wider theory which is here introduced, gives an insight into the co-ordinating power of the more comprehensive lines of development which the book describes.

The exposition is throughout clear and interesting. The subject matter provides one more example of the way in which mathematics covers the domains of abstract thought with ideas of ever increasing generality.

Introduction to the Mathematical Theory of the Conduction of Heat in Solids. By H. S. CARSLAW, Professor of Mathematics in the University of Sydney, formerly Fellow of Emmanuel College, Cambridge. (Macmillan & Co. 2nd Edition, 30*s*. net. 1921.)

THE first edition of the work, entitled 'Fourier's Series and Integrals and the Mathematical Theory of the Conduction of Heat,' was first published in 1906. A new edition of the part dealing with Fourier's Series and Integrals was issued early in 1921, and the present volume forms a new and revised account of the part dealing with the Conduction of Heat. There are various additions to the subject matter, including a discussion of all the important boundary conditions associated with the Equation of Conduction, which is of interest also to those who are concerned with the application of modern analysis to the solution of the differential equations of mathematical physics. We also remark the inclusion of new matter in the chapters which deal with the sphere and cone, the circular cylinder, and the chapter about Green's theorem, amongst others.

Beyond the many minor improvements which make this new issue of the work of 1906 of added value, the considerable additions and the inclusion of a large amount of new material make it of real importance as a new work.

The Aggregation and Flow of Solids. By Sir GEORGE BEILBY. Pp. xv + 256. Macmillan. Price 20*s*. net.

IN this book Sir George Beilby has collected together the very interesting work which he has carried out during the past twenty years on the coexistence of the amorphous and the crystalline states in solids, and the relative influence of the two modifications on the mechanical and other physical properties of metals. He has worked away from the beaten track: the problems which he attacks receive little attention in the ordinary text-books on the properties of matter, although they are of great interest to the physicist as well as to the metallurgist. The study of the optical properties of thin metal leaf, to which he contributes some instructive experiments, has received little attention since the time of Faraday. His careful work on the hardening by wire-drawing, and the effect of annealing hard-drawn metals at different temperatures—work which incidentally brings out a close parallelism between the thermoelectric force against a standard metal and the mechanical strength of the metal in its different modifications, and so indicates the importance of the thermoelectric force as an index of the change of state—simplifies a complex problem of considerable practical importance which was long neglected in this country. The extreme hardness of the amorphous phase and the effect of dissolved gases on the crystalline state are noteworthy facts which are well brought out by experiment.

Sir George Beilby's best known work is, perhaps, that on the nature of polish, in which he showed that the effect of polishing is to flow a thin layer of hard amorphous material over the otherwise crystalline surface of the solid. His beautiful coloured photographs showing how a film of the amorphous modification, thin enough to be transparent, can be actually made to flow over empty pits in the surface of copper by the process of polishing are reproduced. The depth of the disturbance produced by polishing, the increased hardness of the surface, and the transmission of the directive action of the crystals through a layer of non-crystalline material were all investigated, and the whole question of polish was put in order. Two other sections of the book deal with the flow of rocks and ice, and the phosphorescence of crystals respectively. The latter shows a certain disregard of work which had been previously carried out by Lenard and others.

The book is beautifully printed and produced, and adorned with over a hundred reproductions of microphotographs printed as thirty-four plates at the end of the book. It is very moderately priced as books go nowadays, and we congratulate Sir George Beilby on having brought together his work in so attractive a form.

The Physical Properties of Colloidal Solutions. By E. F. BURTON. Pp. viii + 221. Second Edition. Longmans. Price 12*s.* 6*d.*

THE second edition of Professor Burton's book contains some twenty pages more than the first, which appeared in 1916. The chapter on Coagulation of Colloids has been rewritten and greatly extended: it now contains a table showing the relative coagulating power of different ions. Changes and additions have been made in other parts of the book, one of the most interesting being the discussion of limitations of Perrin's distribution law, which is known not to hold for large depths; in such cases there is a limiting concentration. By taking into account the charge on the colloidal particles a correction term is introduced. Perrin's original formula was applicable, however, to such conditions as he employed, and his numerical results are not questioned. The book is warmly recommended.

Series Spectra. By NORMAN R. CAMPBELL. Pp. viii + 110. Cambridge University Press. Price 10*s.* 6*d.* net.

THE second edition of Dr. Campbell's well-known 'Modern Electrical Theory,' which appeared early in 1913, is now necessarily largely out of date—the theories described are now no longer, in many cases, modern. The author has decided not to issue a fresh edition, but to supplement the book by a series of monographs dealing with the branches of the subject which have been most affected by the work of the past nine years. The modern electrical theory of spectra has been entirely developed during this period, so that Dr. Campbell has naturally decided to devote his first monograph to that subject. There were fourteen chapters in his book; consequently the book before us is entitled Modern Electrical Theory, Chapter XV.

Dr. Campbell's book is really needed, and he has acquitted himself well of the very difficult task before him—to describe in some hundred pages the experimentally established regularities of series spectra, and the explanation of them on the lines first indicated by Bohr, when he showed how the series formulæ for hydrogen and helium could be derived by an application of the quantum theory to Rutherford's nucleus atom.

Bohr's fundamental theory of stable non-radiating orbits is well-known to readers of this magazine, where the papers describing it were first published; it has been considerably extended by Sommerfeld, Kossel, and especially by Bohr himself. Dr. Campbell begins by describing briefly the properties of series, laying particular stress on the Principle of Combination, which, of course, finds so simple an explanation on Bohr's theory, and indicating the bearing of the ionization potential. After having outlined, then, the fundamental facts which call for explanation he gives an account of Bohr's early theory, with circular orbits, in all its applications. He next deals with conditionally periodic orbits, the Zeeman and the Stark effect, and Sommerfeld's explanation of the fine structure of the hydrogen and helium lines by applying the relativity correction to the motion in the orbits. After this he passes to the question of intensity of the lines, and treats of the correspondence principle, which has assumed such great importance in Bohr's latest work, which had been only hinted at when the book was published. The book closes with a brief discussion of band spectra, the study of which may be anticipated to give important results in the near future.

In general the treatment is excellent. The discussion of the experimental facts might have been a little fuller, but the reader seeking more information can now turn to Professor Fowler's 'Report on Series in Line Spectra,' which has just appeared, and should be read in conjunction with Dr. Campbell's book. The correspondence principle is not as clearly expounded as could be wished, which is regrettable in view of its increasing application. We note with sorrow a large number of misprints, of which, perhaps, the most serious and inexplicable is $6{\cdot}17 \times 10^4$ printed instead of $8{\cdot}42 \times 10^4$ as the frequency for mercury vapour on p. 24. A statement that there is only one electron in the inner ring is an obvious slip. The positive merits of the book undoubtedly outweigh very heavily any minor defects, and if it does not achieve the extensive circulation which it certainly merits, the rather high price set on it by the publishers rather than any fault of the author's will be the cause.

Moderne Magnetik. By FELIX AUERBACH. Pp. viii + 304.
Leipsig: J. A. Barth, 1921. Price 55 M.

THIS book gives a remarkably comprehensive account of magnetism in all its bearings. The properties of magnets and ferromagnetic bodies, and of the various methods employed for measuring the strength of magnetic fluids and the permeability of specimens, are expounded in a clear and logical manner, all practical experimental devices, including Lenard's bismuth spiral, being described, if only in outline. This is the ground covered in more detail in Ewing's well-known book, but much matter which has appeared since the date of that work finds reference here. In addition we have chapters devoted to the effect of mechanical deformation (tension, torsion, and so on) on magnetic properties, to magneto-optics, to recent theories, and to phenomena connected with terrestrial magnetism. The last mentioned contains an all too brief account of Birkeland's and Störmer's beautiful work on the aurora, with a few of their pictures. The modern electron theories of magnetism of Gans, Langevin, and Weiss are ably expounded, but no reference is made to the bearing of Bohr's work on the Zeeman effect, Voigt's theory of the effect, which has had no outstanding success, being given instead.

It will be seen that a great deal of modern work, which has not yet found its way into the ordinary English text-books, has been compressed into this book. On account of the very wide scope no detailed treatment is possible, and intriguing phenomena, such as those exhibited by the Heusler alloys, are dismissed in a couple of pages. This is inevitable in a book of this size, and is not mentioned as a hostile criticism. Considering the limits which the author has set himself, everything is very clearly treated. The book is written in a pleasant, human, and picturesque style, with considerably more liveliness than a German scientist usually allows himself. There is an amusing digression on text-books at the beginning of Chapter IX. We commend this book, and think that many readers of the Philosophical Magazine will find it useful.

CXXII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 640.]

December 21st, 1921.—Mr. R. D. Oldham, F.R.S., President, in the Chair.

THE following communications were read :—

1. 'The Nature and Origin of the Pliocene Deposits of the County of Cornwall and their bearing on the Pliocene Geography of the South-West of England.' By Henry Brewer Milner, M.A., D.I.C., F.G.S.

The author discusses the petrography of those Tertiary deposits of Cornwall which, by reason of similar mode of occurrence and lithological resemblance to the well-known fossiliferous beds of St. Erth, have been provisionally assigned to the Pliocene Period. Such deposits occur at St. Agnes, St. Erth, Lelant Downs, Polcrebo, and St. Keverne; except those of St. Erth, all are unfossiliferous.

By petrographic methods of correlation, using St. Erth as a type-locality, the relative age of the St. Agnes and St. Keverne beds is established. At Lelant Downs no deposit occurs *in situ*, but scattered blocks of an indurated ferruginous grit are found at an elevation corresponding to that of the St. Erth beds on the opposite side of the valley, and a potential relationship is accordingly admitted. The Polcrebo gravels differ from the other deposits, and are referred to a later period.

The average composition of the St. Agnes, St. Erth, and St. Keverne deposits is shown to be substantially the same, the important 'heavy' minerals common to all being magnetite, ilmenite, tourmaline, staurolite, epidote, zircon, anatase, rutile, topaz, andalusite, and cassiterite; garnet was found only at St. Erth, kyanite at St. Agnes and St. Erth. On this basis, correlation of the deposits is effected by considering (1) the frequency of occurrence of individual species; (2) their persistence or distribution; and (3) the constancy of crystallographical, physical, and optical properties of grains of the same mineral, wherever met with.

The source of the material is essentially local, although kyanite and staurolite are 'foreign' species; the former, from its striking Lower Greensand habit and absence from St. Keverne, is thought to be derived from the north-east, the latter from a land-mass lying on the south, probably united to Cornwall and

Devon in late Miocene times, before early Pliocene submergence set in. The gradual 'swamping' of sediment-bearing rivers by the advancing Pliocene sea from the south-west is correlated with certain physical features apparent, especially the '400-foot plateau.'

2. 'The Phosphate Deposit of Ocean Island.' By Launcelot Owen, A.R.S.M., A.R.C.S., F.G.S.

Ocean Island (lat. 0° 52′ S.; long. 169° 32′ E.), in the Western Pacific Ocean, consists of a mass of terraced and dolomitized coral-limestone which rises to a height of 300 feet above low water, spring tide.

Its surface is almost completely covered by a capping of calcium phosphate of exceptional purity. This phosphate can be divided into three varieties:—(*a*) amorphous calcium phosphate, formed of the insoluble residue of the original guano; (*b*) detrital coral-limestone, converted into calcium phosphate by solutions leached from the guano; and (*c*) phosphatized coral *in situ.*

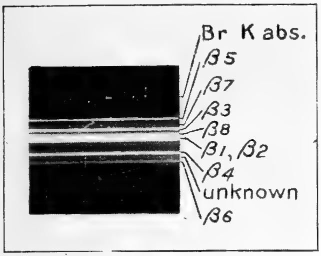
The dolomitized limestone base shows evidence of having suffered considerable subaërial and marine erosion prior to the deposition of the guano, this deposition having occurred during the final emergence of the island.

A detailed study of the composition of the deposit shows that the percentage of tricalcium phosphate ($Ca_3P_2O_8$) at any point varies in a remarkably regular manner, according to the position of the point on the island. So regular is this variation, in fact, that, if the position and height above sea-level of any point are known, the percentage of tricalcium phosphate in the deposit at that point can be foretold with considerable accuracy.

The trend of this variation suggests that:—(*a*) the original guano was deposited on the coral base while a slow negative movement of the strand-line was in progress, and no sensible break occurred either in the deposition of the guano, or in the movement of emergence; (*b*) subsequent to the deposition of the guano and its conversion into phosphate, the island was tilted at about a third of a degree south-south-eatwards. This supposition is strengthened by the occurrence of raised beaches in the north of the island, and of phosphate *in situ* below sea-level on the south.

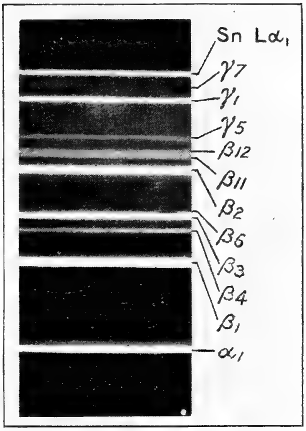
A study of similar deposits may help to throw some light on the post-Tertiary movements of the floor of the Pacific Ocean.

Fig. 1.



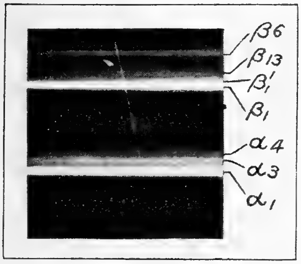
Pb $L\beta$ (rocksalt crystal).

Fig. 2.



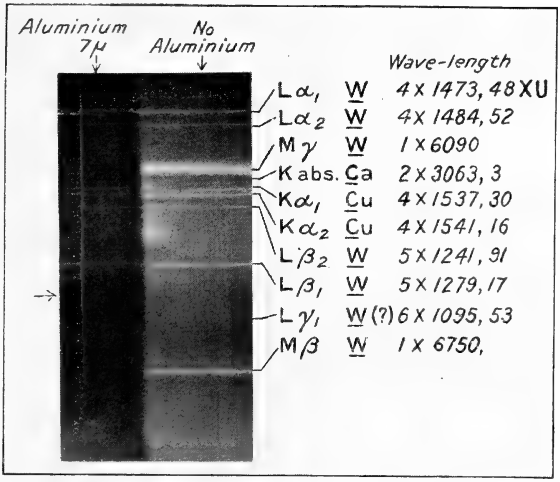
Rh L-spectrum (gypsum crystal).

Fig. 3.

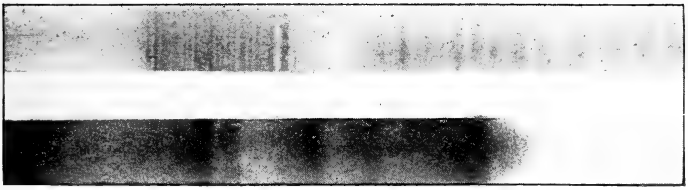


Rb $L\alpha_1$ and $L\beta_1$ with their satellites (gypsum crystal).

Fig. 4.



W L and M spectrum (gypsum crystal).



Low
Velocity
High
Velocity.

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END OF THE FORTY-THIRD VOLUME.

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