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ADVERTISEMENT.

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SERIES A, VOL. 208, pp. 1–19.

FURTHER CONSIDERATION OF THE STABILITY OF THE PEAR-SHAPED FIGURE OF A ROTATING MASS OF LIQUID

BY

SIR G. H. DARWIN, K.C.B, F.R.S.,
PLUMIAN PROFESSOR OF ASTRONOMY, AND FELLOW OF TRINITY COLLEGE, CAMBRIDGE.

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PHILOSOPHICAL TRANSACTIONS.

I. *Further Consideration of the Stability of the Pear-shaped Figure of a Rotating Mass of Liquid.*

By Sir G. H. Darwin, *K.C.B., F.R.S., Plumian Professor of Astronomy, and Fellow of Trinity College, Cambridge.*

Received October 29,—Read December 12, 1907.

Introduction.

In vol. 17, No. 3 (1905), of the 'Memoirs of the Imperial Academy of St. Petersburg,' M. Liapounoff has published an abstract of his work on figures of equilibrium of rotating liquid under the title "Sur un Problème de Tchebychef." In this paper he explains how he has obtained a rigorous solution for the figure and stability of the pear-shaped figure, and he pronounces it to be unstable. In my paper in the 'Philosophical Transactions'* I had arrived at an opposite conclusion.

The stability or instability depends, in fact, on the sign of a certain function which M. Liapounoff calls A, and which I denote $A_0+\Sigma(B_i^s)^2/C_i^s$, where A_0 is equal to $\mathfrak{A}_3[\frac{1}{3}(\sigma_2)^2+2\zeta_1]-\frac{1}{3}\sigma_4+\Sigma[i, s]$.

M. Liapounoff tells us that, after having seen my conclusion he repeated all his computations and confirmed his former result. He attributes the disagreement between us to the fact that I have only computed portion of an infinite series, and only used approximate forms for the elliptic integrals in the several terms. He believes that the inclusion of the neglected residue of the infinite series would lead to an opposite conclusion.

In my computation the function $\mathfrak{A}_3[\frac{1}{3}(\sigma_2)^2+2\zeta_1]-\frac{1}{3}\sigma_4$ is decisively negative, and being numerically greater than $\Sigma\{(B_i^s)^2/C_i^s+[i, s]\}$, which is positive, the sum of the two is negative. The inclusion of the neglected residue undoubtedly tends to make this whole function positive, but after making the revision, explained in the present paper, it remains incredible, to me at least, that the neglected residue can amount to the total needed to invert the sign.

It may be worth mentioning that in revising my work I notice that $\mathfrak{A}_3[\frac{1}{3}(\sigma_2)^2+2\zeta_1]-\frac{1}{3}\sigma_4$ owes its negative sign to the term $-\frac{1}{3}\sigma_4$. This term arises from the energy of the double layer, called $\frac{1}{2}$DD. It comes from the portion of the term $\frac{2}{3}\pi\rho^2\int\epsilon^3(1-\lambda\epsilon)\,d\sigma$, which gives rise to a term in e^4 with a negative sign. This

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* Series A, vol. 200, pp. 251–314.

term involves under the integral sign the factor $\frac{5}{2}\left(\frac{1}{\Gamma_1^2}+\frac{1}{\Delta_1^2}\right)-3G$, all the other factors being positive. If we attribute to θ and to ϕ various values between $\frac{1}{2}\pi$ and zero, we see that in part of the range the factor is positive and in other parts negative. A general inspection does not suffice to determine whether the positive portion outweighs the negative, as in fact it does. Therefore, in order to feel abundantly sure that no gross mistake had been made, I computed by quadratures the eight constituent integrals involved in the final result, and confirmed the correctness of the value found by the rigorous evaluation.

The analysis of the investigation has been carefully examined throughout, and I have, besides, applied the same method to the investigation of MACLAURIN'S spheroid, where the solution can be verified by the known exact result.*

As a further check, the formulæ of the paper on the Pear-shaped Figure have been examined on the hypothesis that the ellipsoid of reference reduces to a sphere. The several terms correctly reproduce the analogous terms in the paper on MACLAURIN'S spheroid, but in effecting the comparison it is necessary to note that the variable τ of the Pear-shaped Figure reduces to $\frac{1}{2}\left(1-\frac{r^2}{a^2}\right)$, whereas in the paper on MACLAURIN'S spheroid the corresponding variable τ denotes $\frac{1}{3}\left(1-\frac{r^3}{a^3}\right)$, where r is radius vector and a the radius of the sphere.

Dissent from so distinguished a mathematician as M. LIAPOUNOFF is not to be undertaken lightly, and I have, as explained, taken especial pains to ensure correctness. Having made my revision, and completed the computations as set forth hereafter, I feel a conviction that the source of our disagreement will be found in some matter of principle, and not in the neglected residue of this series. I can now only express a hope that some one else will take up the question.

In the revision of the computations, the methods now used are much better than the old ones. In as far as this paper is a mere repetition of the former work with improved methods, the results will only be stated in outline, but I now show how any of the ellipsoidal harmonic functions may be computed without approximation, and how the functions of the second kind may be found rigorously.

The Cambridge University Press is now bringing out a collection of my mathematical papers, and when we come to the paper on the stability of the pear-shaped figure, the new methods of computation will be substituted for the old.

This paper is supplementary to the former one on Stability,† and it will only be intelligible in connection therewith. As before, I refer to the papers in the 'Philosophical Transactions'‡ as "Harmonics" and the "Pear-shaped Figure."

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* 'Amer. Math. Soc. Trans.,' 1903, vol. 4, p. 113, on "The Approximate Determination of the Form of MACLAURIN'S Spheroid," and a further note on the same subject, recently sent to the same Society.

† 'Phil. Trans.,' A, vol. 200, p. 251.

‡ Vol. 197, A, p. 461, and vol. 198, A, p. 301.

§ 1. *The Rigorous Expression for the Ellipsoidal Harmonic Functions.*

Rigorous forms have been found in previous papers for all the harmonics of orders up to the third inclusive. For harmonics of the fourth order rigorous algebraic forms may be obtained in all cases except when $s = 0, 2, 4$, but these are exactly the cases to be considered in this investigation. We have, then, to show how these functions of higher orders may be evaluated rigorously for an ellipsoid of known ellipticity.

The only case required is that in which both i and s are even, and although all the forms might be evaluated by processes similar to those indicated below, I shall confine myself to this case.

We have seen in "Harmonics" that if β denotes $(1-\kappa^2)/(1+\kappa^2)$ of this paper, and μ denotes $\sin\theta$,

$$\begin{aligned}\mathfrak{P}_i^s(\mu) = P_i^s(\mu) - \beta q_{s+2} P_i^{s+2}(\mu) + \beta^2 q_{s+4} P_i^{s+4}(\mu) - \ldots + (-)^{\frac{1}{2}(i-s)} \beta^{\frac{1}{2}i} q_i P_i^i(\mu) \\ - \beta q_{s-2} P_i^{s-2}(\mu) + \beta^2 q_{s-4} P_i^{s-4}(\mu) - \ldots + (-)^{\frac{1}{2}s} \beta^{\frac{1}{2}s} q_0 P_i(\mu).\end{aligned}$$

It is well known that

$$P_i(\mu) = \frac{1}{2^i i!} \frac{d^i}{d\mu} (\mu^2-1)^i,$$

and

$$\begin{aligned}P_i^s(\mu) = \frac{(i+s)(i+s-1)\ldots(i-s+1)}{2^s \,.\, s!} (1-\mu^2)^{\frac{1}{2}s} \Big[\mu^{i-s} - \frac{(i-s)(i-s-1)}{1!\,2^2(s+1)} \mu^{i-s-2}(1-\mu^2) \\ + \frac{(i-s)(i-s-1)(i-s-2)(i-s-3)}{2!\,2^4(s+1)(s+2)} \mu^{i-s-4}(1-\mu^2)^2 - \ldots\Big].\end{aligned}$$

Hence we may clearly write $\mathfrak{P}_i^s$ in the form

$$\mathfrak{P}_i^s(\mu) = f_0 \sin^i\theta - f_2 \sin^{i-2}\theta \cos^2\theta + f_4 \sin^{i-4}\theta \cos^4\theta - \ldots.$$

Since when s is not zero $P_i^s(1) = 0$, and when s is zero $P_i(1) = 1$, it follows that $f_0 = (-)^{\frac{1}{2}s} \beta^{\frac{1}{2}s} q_0$. For the zonal harmonics $(s = 0)$ this gives $f_0 = 1$. The determination of the other f's depends on that of the q's, which we shall consider later.

Another form of $\mathfrak{P}_i^s(\mu)$ will be useful, viz.:

$$\mathfrak{P}_i^s(\mu) = a - b\cos^2\theta + c\cos^4\theta - d\cos^6\theta + e\cos^8\theta - \ldots.$$

It is obvious that

$$\begin{aligned} a &= f_0, \\ b &= f_2 + \frac{i}{2\,.\,1!} f_0, \\ c &= f_4 + \frac{i-2}{2\,.\,1!} f_2 + \frac{i(i-2)}{2^2\,.\,2!} f_0, \\ d &= f_6 + \frac{i-4}{2\,.\,1!} f_4 + \frac{(i-2)(i-4)}{2^2\,.\,2!} f_2 + \frac{i(i-2)(i-4)}{2^3\,.\,3!} f_0, \\ &\&\text{c.}, \qquad \&\text{c.}, \qquad \&\text{c.} \end{aligned}$$

Thus, when the f's are computed it is easy to obtain the a, b, c, d, &c.

We know that $\mathfrak{C}_i^s(\phi)$ (the cosine function of ϕ) is the same function of $-\kappa'^2 \sin^2\phi$ that $\mathfrak{P}_i^s(\mu)$ is of $\kappa^2\cos^2\theta$, except as regards a constant factor.

Hence it follows that

$$\mathfrak{C}_i^s(\phi) = \lambda\left[a + b\frac{\kappa'^2}{\kappa^2}\sin^2\phi + c\frac{\kappa'^4}{\kappa^4}\sin^4\phi + d\frac{\kappa'^6}{\kappa^6}\sin^6\phi + \ldots\right],$$

where λ is a constant factor.

Now I desire to define $\mathfrak{P}_i^s(\mu)$ and $\mathfrak{C}_i^s(\phi)$ exactly as in "Harmonics."

This definition has already been adopted as regards $\mathfrak{P}_i^s(\mu)$, but it remains to adjust the constant λ so as to attain the same end as regards $\mathfrak{C}_i^s(\phi)$.

When i and s are even, $\mathfrak{C}_i^s(\phi)$ was defined thus:

$$\mathfrak{C}_i^s(\phi) = \cos s\phi + \beta p_{s+2}\cos(s+2)\phi + \beta^2 p_{s+4}\cos(s+4)\phi + \ldots + \beta^{\frac{1}{2}(i-s)}p_i\cos i\phi$$
$$+\beta p_{s-2}\cos(s-2)\phi + \beta^2 p_{s-4}\cos(s-4)\phi + \ldots + \beta^{\frac{1}{2}s}p_0.$$

Since

$$\sin^{2r}\phi = \frac{2r\,!}{2^{2r}(r\,!)^2} - \frac{2r\,!}{2^{2r-1}(r-1)\,!\,(r+1)\,!}\cos 2\phi + \frac{2r\,!}{2^{2r-1}(r-2)\,!\,(r+2)\,!}\cos 4\phi - \ldots,$$

it follows that the term independent of ϕ in $\mathfrak{C}_i(\phi)$ is

$$\lambda\left[a + \tfrac{1}{2}b\frac{\kappa'^2}{\kappa^2} + \frac{1\,.\,3}{2\,.\,4}c\frac{\kappa'^4}{\kappa^4} + \frac{1\,.\,3\,.\,5}{2\,.\,4\,.\,6}d\frac{\kappa'^6}{\kappa^6} + \ldots\right].$$

The term in $\cos 2\phi$ in $\mathfrak{C}_i^2(\phi)$ is

$$-2\lambda\cos 2\phi\left[\frac{1}{2}\,.\,\frac{1}{2}\,b\frac{\kappa'^2}{\kappa^2} + \frac{1\,.\,3}{2\,.\,4}\,.\,\frac{2}{3}\,c\frac{\kappa'^4}{\kappa^4} + \frac{1\,.\,3\,.\,5}{2\,.\,4\,.\,6}\,.\,\frac{3}{4}\,d\frac{\kappa'^6}{\kappa^6} + \ldots\right].$$

The term in $\cos 4\phi$ in $\mathfrak{C}_i^4(\phi)$ is

$$2\lambda\cos 4\phi\left[\frac{1\,.\,3}{2\,.\,4}\cdot\frac{1\,.\,2}{3\,.\,4}\,c\frac{\kappa'^4}{\kappa^4} + \frac{1\,.\,3\,.\,5}{2\,.\,4\,.\,6}\cdot\frac{2\,.\,3}{4\,.\,5}\,d\frac{\kappa'^6}{\kappa^6} + \frac{1\,.\,3\,.\,5\,.\,7}{2\,.\,4\,.\,6\,.\,8}\cdot\frac{3\,.\,4}{5\,.\,6}\,e\frac{\kappa'^8}{\kappa^8} + \ldots\right],$$

and so forth.

In accordance with the definition to be adopted, these terms in the three cases respectively are: 1, $\cos 2\phi$, $\cos 4\phi$. Hence λ must be chosen so as to fulfil that condition.

Pursuing only the case of $\mathfrak{C}_i(\phi)$ in detail, we have

$$\frac{1}{\lambda} = a + \tfrac{1}{2}b\frac{\kappa'^2}{\kappa^2} + \frac{1\,.\,3}{2\,.\,4}c\frac{\kappa'^4}{\kappa^4} + \ldots.$$

If, then,

$$\mathfrak{C}_i(\phi) = a'+b'\sin^2\phi+c'\sin^4\phi+\dots,$$

we must have

$$a' = \lambda a, \quad b' = \lambda b\frac{\kappa'^2}{\kappa^2}, \quad c' = \lambda c\frac{\kappa'^4}{\kappa^4}, \quad \text{\&c.}$$

Thus when f_0, f_2, f_4, &c., are found, it is easy to compute a, b, c, &c., and a', b', c', &c.

Our formulæ tend to involve the differences between large numbers, and this defect becomes more pronounced as the order of harmonics increases. The fault is mitigated by using the forms

$$\mathfrak{P}_i(\mu) = f_0\sin^i\theta - f_2\sin^{i-2}\theta\cos^2\theta+\dots,$$

$$\mathfrak{C}_i(\phi) = a'+b'\sin^2\phi+c'\sin^4\phi+\dots.$$

In the case of a lower harmonic, however, such as the fourth, we may just as well use the form for $\mathfrak{P}$ involving a, b, c, &c., and powers of $\cos^2\theta$.

We must now show how to complete the evaluation of the f's for the zonal harmonics.

It appears, from p. 486 of "Harmonics," that, when i is even, we have to solve the equation

$$\beta\sigma = \frac{\frac{1}{2}\beta^2\{i, 1\}\{i, 2\}}{4 . 1^2+\beta\sigma-}\;\frac{\frac{1}{4}\beta^2\{i, 3\}\{i, 4\}}{4 . 2^2+\beta\sigma-\dots},$$

ending with

$$\frac{-\frac{1}{4}\beta^2\{i, i\}\{i, i-1\}}{i^2+\beta\sigma}; \quad \text{where} \quad \{i, j\} = (i+j)(i-j+1).$$

We are to take that root which vanishes when β vanishes.

Although the equation for $\beta\sigma$ is of order $i-1$, yet at least for such an ellipsoid as we have to deal with, it is very easy to solve it by successive rapid approximations.

It is clear that we may write the equation in the form

$$(\beta\sigma)^2+\left[4-\frac{\frac{1}{4}\beta^2\{i, 3\}\{i, 4\}}{4 . 2^2+\beta\sigma-}\;\frac{\frac{1}{4}\beta^2\{i, 5\}\{i, 6\}}{4 . 3^2+\beta\sigma-\dots}\right]\beta\sigma = \tfrac{1}{2}\beta^2\{i, 1\}\{i, 2\}.$$

An analytical approximation is found by neglecting the continued fraction in the second term on the left, and we then obtain

$$\beta\sigma = -2+2\sqrt{[1+\tfrac{1}{8}\beta^2(i-1)i(i+1)(i+2)]}.$$

If this value of $\beta\sigma$ is used in computing the first term of the continued fraction, and if the quadratic is solved again, we obtain a closer approximation. We then use the second approximation and include one more term in the continued fraction, and proceed until $\beta\sigma$ no longer changes.

It is shown on pp. 486, 487 of "Harmonics" that

$$\frac{q_2}{q_0} = \frac{1}{4\,.\,1^2+\beta\sigma-}\;\frac{\frac{1}{4}\beta^2\{i,3\}\{i,4\}}{4\,.\,2^2+\beta\sigma-\dots},$$

$$\frac{2q_4}{q_2} = \frac{1}{4\,.\,2^2+\beta\sigma-}\;\frac{\frac{1}{4}\beta^2\{i,5\}\{i,6\}}{4\,.\,3^2+\beta\sigma-\dots},$$

$$\frac{2q_6}{q_4} = \frac{1}{4\,.\,3^2+\beta\sigma-}\;\frac{\frac{1}{4}\beta^2\{i,7\}\{i,8\}}{4\,.\,4^2+\beta\sigma-\dots},$$

. . . .

It may be remarked that the factor 2 occurs in each of these equations on the left, excepting in the first one; also we are to take $q_0 = 1$.

In the course of the successive approximations for the determination of $\beta\sigma$, each of these fractions is naturally evaluated. Therefore it is only necessary to extract certain numerical values already found in the course of solving the equation for $\beta\sigma$.

As a verification, which shows whether the equation has been correctly solved, we have

$$\frac{q_0}{q_2} = \frac{\frac{1}{2}\beta^2\{i,1\}\{i,2\}}{\beta\sigma}.$$

It is now obvious that we are able to find all the q's in terms of q_0, which is unity. We then multiply each q by its appropriate power of β or $\frac{1-\kappa^2}{1+\kappa^2}$, that is to say, we form $\beta^r q_{2r}$ for $r = 1, 2, \dots, \frac{1}{2}i$, and introduce the results into the formula for $\mathfrak{P}_i(\mu)$.

A closely analogous method enables us to find all the other types of function for an ellipsoid of known ellipticities, but, except for certain harmonics of the fourth order, it is not possible to obtain rigorous analytical solutions. Approximate analytical forms are given in "Harmonics," and the approximation may be carried further if desired.

The following tables give the coefficients in the several functions for the critical Jacobian ellipsoid with which we are dealing:—

i.	*s.*	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*
*2 *2	0 2	0·603374 −0·039203	0·923128 0·923128				
4 4 4	0 2 4	1·000000 1·769147 0·083965	5·442161 −36·154264 − 7·984389	4·892138 −44·93584 95·562431			
6 †6 †6	0 2 4	1·000000 −8·4 3·78	12·45814 121·8 −338·312	29·55340 439·425 3680·303	18·53561 320·523 4482·844		
8	0	1·00000	23·29297	103·90805	155·9554	74·7977	
10	0	1·00000	38·29978	274·94458	721·88640	789·90216	306·12784

i.	*s.*	*a′.*	*b′.*	*c′.*	*d′.*	*e′.*	*f′.*
*2 *2	0 2	0·603374 −0·039203	0·076872 0·076872				
4 4 4	0 2 4	0·806905 1·065020 1·013640	0·365661 −1·812415 −8·026680	0·027371 −0·187586 8·000000			
6 †6 †6	0 2 4	0·62544 −1·1408 1·0305	0·64882 1·5349 −7·704	0·12816 0·4404 6·944	0·00669 0·0264 0·704		
8	0	0·440664	0·854891	0·317488	0·396793	0·001585	
10	0	0·289818	0·924288	0·552512	0·120795	0·011006	0·000355

* The second harmonics are here defined by $\mathfrak{P}_2^s(\mu) = \kappa^2 - q_s^2 - \kappa^2 \cos^2 \theta$, $\mathfrak{C}_2^s = \kappa^2 - q_s^2 + \kappa'^2 \sin^2 \phi$ $(s = 0, 2)$ with $q_s^2 = \frac{1}{3}[1 + \kappa^2 \mp \surd(1 - \kappa^2\kappa'^2)]$, with the upper sign for $s = 0$ and the lower for $s = 2$. In the case of $i = 4$, $s = 2$, I had in the original paper inadvertently changed the sign *both* of $\mathfrak{P}_4^2$ and $\mathfrak{C}_4^2$ without, of course, introducing any error, since they occur always as a product.

† These functions are only given in their approximate forms.

As it is desirable to use the other form of $\mathfrak{P}$ in the higher zonal harmonics, I give the coefficients f_0, f_2, f_4, &c., in these cases. It will be noticed how much smaller are the numbers involved.

COEFFICIENTS of Terms in $\mathfrak{P}_i(\mu)$ when expressed in Sines and Cosines.

i.	s.	f_0.	f_2.	f_4.	f_6.	f_8.	f_{10}.
6	0	1·00000	9·45814	7·63713	0·44035		
8	0	1·00000	19·29797	40·01416	14·03323	0·45235	
10	0	1·00000	33·29978	131·74546	116·85134	22·76398	0·46728

§ 2. *The Rigorous Expression for the Harmonics of the Second Kind.*

The integral $\mathfrak{A}_i^s$ denotes $\mathfrak{P}_i^s(\nu_0)\,\mathfrak{Q}_i^s(\nu_0)$, and $\mathfrak{B}_i^s$ denotes $\mathfrak{Q}_i^s(\nu_0)\dfrac{d}{d\nu_0}\mathfrak{P}_i^s(\nu_0)$. Thus $\mathfrak{A}_i^s$ is, in fact, the harmonic function of the second kind. $\mathfrak{B}_i^s$ is clearly determinable from $\mathfrak{A}_i^s$.

In the original paper $\mathfrak{A}_i^s$ was found by quadrature, and this defect in my procedure is referred to by M. LIAPOUNOFF as a cause possibly contributory to the discrepancy between our results. Quadrature was not, perhaps, a very satisfactory method, and the defect will now be made good by finding these integrals in terms of the F and E elliptic integrals. It will appear that my former results were sufficiently near to the truth for practical purposes.

The functions $\mathfrak{P}_i^s(\nu)$ or $\mathsf{P}_i^s(\nu)$ are of eight types, determined by the oddness or evenness of i and s, and the association with a cosine or sine function of ϕ. In "Harmonics" the types are indicated by combinations in groups of three of the four letters E, O, C, S—denoting Even, Odd, Cosine, Sine; for example, OES means i odd, s even, associated with a sine function.

All the roots of the equation $\mathfrak{P}_i^s(\nu)$ or $\mathsf{P}_i^s(\nu) = 0$ are real, and when the form of the function has been determined by the method of § 1 the equation may be solved. Hence these functions are expressible as the products of a number of factors; and it is to be noted that it is not necessary to adopt the same definition as in "Harmonics," because the function may be multiplied by any constant factor, without affecting the result.

For brevity, let

$$\prod_1^n(\kappa^2\nu^2-q_x^2) = (\kappa^2\nu^2-q_1^2)(\kappa^2\nu^2-q_2^2)\ldots(\kappa^2\nu^2-q_n^2),$$

where κ^2 is $(1-\beta)/(1+\beta)$ of "Harmonics." The parameters, κ and γ, as elsewhere, define the form of the ellipsoid.

An alternative notation will be needed, in which we write

$$\nu^2 = \frac{1}{\kappa^2\sin^2\psi}, \quad \Delta_x^2 = 1-q_x^2\sin^2\psi, \quad \Delta^2 = 1-\kappa^2\sin^2\psi.$$

At the surface of the ellipsoid $\nu = \nu_0$, $\psi = \gamma$, and we shall, as before, write $\sin\beta = \kappa \sin\gamma$. At the surface of the ellipsoid we have then

$$\nu = \operatorname{cosec}\beta, \quad \Delta_x^2 = 1 - q_x^2 \sin^2\gamma, \quad \Delta^2 = \cos^2\beta.$$

In this notation

$$\prod_1^n \left(\frac{\Delta_x^2}{\sin^2\psi}\right) = \frac{\Delta_1^2 \Delta_2^2 \ldots \Delta_n^2}{\sin^{2n}\psi}.$$

A consideration of the eight types of harmonics shows that they may be written as follows :—

Type.

$$\begin{array}{lllll}
\text{EEC}, & \mathfrak{P}_{2n}^{2t}(\nu) & = \prod_1^n (\kappa^2\nu^2 - q_x^2) & = \operatorname{cosec}^{2n}\psi \prod_1^n (\Delta_x^2), \\
\text{EES}, & \mathsf{P}_{2n+2}^{2t}(\nu) & = (\kappa^2\nu^2 - \kappa^2)^{\frac{1}{2}} (\kappa^2\nu^2 - 1)^{\frac{1}{2}} \prod_1^n (\kappa^2\nu^2 - q_x^2) & = \operatorname{cosec}^{2n+2}\psi\, \Delta \cos\psi \prod_1^n (\Delta_x^2), \\
\text{OOC}, & \mathsf{P}_{2n+1}^{2t+1}(\nu) & = (\kappa^2\nu^2 - 1)^{\frac{1}{2}} \prod_1^n (\kappa^2\nu^2 - q_x^2) & = \operatorname{cosec}^{2n+1}\psi \cos\psi \prod_1^n (\Delta_x^2), \\
\text{OOS}, & \mathfrak{P}_{2n+1}^{2t+1}(\nu) & = (\kappa^2\nu^2 - \kappa^2)^{\frac{1}{2}} \prod_1^n (\kappa^2\nu^2 - q_x^2) & = \operatorname{cosec}^{2n+1}\psi\, \Delta \prod_1^n (\Delta_x^2), \\
\text{OEC}, & \mathfrak{P}_{2n+1}^{2t}(\nu) & = \kappa\nu \prod_1^n (\kappa^2\nu^2 - q_x^2) & = \operatorname{cosec}^{2n+1}\psi \prod_1^n (\Delta_x^2), \\
\text{OES}, & \mathsf{P}_{2n+3}^{2t}(\nu) & = \kappa\nu (\kappa^2\nu^2 - \kappa^2)^{\frac{1}{2}} (\kappa^2\nu^2 - 1)^{\frac{1}{2}} \prod_1^n (\kappa^2\nu^2 - q_x^2) & = \operatorname{cosec}^{2n+3}\psi\, \Delta \cos\psi \prod_1^n (\Delta_x^2), \\
\text{EOC}, & \mathsf{P}_{2n+2}^{2t+1}(\nu) & = \kappa\nu (\kappa^2\nu^2 - 1)^{\frac{1}{2}} \prod_1^n (\kappa^2\nu^2 - q_x^2) & = \operatorname{cosec}^{2n+2}\psi \cos\psi \prod_1^n (\Delta_x^2), \\
\text{EOS}, & \mathfrak{P}_{2n+2}^{2t+1}(\nu) & = \kappa\nu (\kappa^2\nu^2 - \kappa^2)^{\frac{1}{2}} \prod_1^n (\kappa^2\nu^2 - q_x^2) & = \operatorname{cosec}^{2n+2}\psi\, \Delta \prod_1^n (\Delta_x^2).
\end{array}$$

Using $\mathfrak{P}$ and $\mathfrak{Q}$ generically for any one of these and for the corresponding function of the other kind, we have

$$\mathfrak{P}(\nu_0)\,\mathfrak{Q}(\nu_0) = [\mathfrak{P}(\nu_0)]^2 \int_{\nu_0} \frac{d\nu}{[\mathfrak{P}(\nu)]^2 (\nu^2-1)^{\frac{1}{2}} (\nu^2 - 1/\kappa^2)^{\frac{1}{2}}}.$$

Or, changing the variable of integration to ψ,

$$\mathfrak{A} = \kappa\,[\mathfrak{P}(\nu_0)]^2 \int_0^\gamma \frac{d\psi}{[\mathfrak{P}(\nu)]^2\,\Delta}.$$

To effect the integration the reciprocal of the square of $\mathfrak{P}$ must be expressed in partial fractions. Inspection of the eight forms of functions shows that

$$\frac{1}{[\mathfrak{P}(\nu)]^2} = \frac{1}{f}\cdot\frac{1}{\kappa^2\nu^2-\kappa^2} + \frac{1}{g}\cdot\frac{1}{\kappa^2\nu^2-1} + \frac{1}{h}\cdot\frac{1}{\kappa^2\nu^2} + \sum_1^n \frac{1}{A_x}\left[\frac{1}{(\kappa^2\nu^2-q_x^2)^3} - \frac{B_x}{\kappa^2\nu^2-q_x^2}\right],$$

with appropriate values of f, g, h, A_x, B_x to be given hereafter.

In every case but that of OES some or all of f, g, h are infinite.

In terms of ψ

$$\frac{1}{[\mathfrak{P}(\nu)]^2} = \frac{1}{f}\frac{\sin^2\psi}{\Delta^2} + \frac{1}{g}\tan^2\psi + \frac{1}{h}\sin^2\psi + \sum_1^n \frac{1}{A_x}\left[\frac{\sin^4\psi}{\Delta_x^{\,4}} - \frac{B_x\sin^2\psi}{\Delta_x^{\,2}}\right].$$

This has to be divided by Δ and integrated, and the result will be expressible in terms of the elliptic integrals

$$F(\gamma) = \int_0^\gamma \frac{d\psi}{\Delta}, \quad E(\gamma) = \int_0^\gamma \Delta\, d\psi, \quad \Pi(\gamma, \Delta_x) = \int_0^\gamma \frac{d\psi}{\Delta_x^{\,2}\Delta}.$$

Accordingly we require certain integrals, which are given on p. 313 of the "Pear-shaped Figure," but in somewhat different forms. Here and elsewhere κ'^2 denotes $1-\kappa^2$, and $q'^{\,2}_x$ denotes $1-q_x^{\,2}$.

The integrals needed are as follows :—

$$\left.\begin{aligned}
\int_0^\gamma \frac{\sin^2\psi}{\Delta^3}\,d\psi &= -\frac{1}{\kappa^2}\,\mathrm{F}(\gamma) + \frac{1}{\kappa^2\kappa'^2}\,\mathrm{E}(\gamma) - \frac{\sin\gamma\cos\gamma}{\kappa'^2\cos\beta} \\
\int_0^\gamma \frac{\tan^2\psi}{\Delta}\,d\psi &= \qquad\qquad -\frac{1}{\kappa'^2}\,\mathrm{E}(\gamma) + \frac{\tan\gamma\cos\beta}{\kappa'^2} \\
\int_0^\gamma \frac{\sin^2\psi}{\Delta}\,d\psi &= \frac{1}{\kappa^2}\,\mathrm{F}(\gamma) - \frac{1}{\kappa^2}\,\mathrm{E}(\gamma)
\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (1)$$

$$\int_0^\gamma \frac{\sin^2\psi}{\Delta_x^{\,2}\Delta}\,d\psi = \frac{1}{q_x^{\,2}}\,\Pi(\gamma, \Delta_x) - \frac{1}{q_x^{\,2}}\,\mathrm{F}(\gamma)$$

$$\begin{aligned}
\int_0^\gamma \frac{\sin^4\psi}{\Delta_x^{\,4}\Delta}\,d\psi = {} & \frac{1}{2q_x^{\,2}}\left(\frac{1}{q'^{\,2}_x} - \frac{1}{q_x^{\,2}} + \frac{1}{\kappa^2-q_x^{\,2}}\right)\Pi(\gamma, \Delta_x) + \frac{1}{2q_x^{\,2}}\left(\frac{1}{q_x^{\,2}} - \frac{1}{q'^{\,2}_x}\right)\mathrm{F}(\gamma) \\
& - \frac{1}{2q_x^{\,2}q'^{\,2}_x(\kappa^2-q_x^{\,2})}\,\mathrm{E}(\gamma) + \frac{\sin\gamma\cos\gamma\cos\beta}{2q'^{\,2}_x(\kappa^2-q_x^{\,2})\,\Delta_x^{\,2}}.
\end{aligned}$$

The last two of these admit of considerable simplification, as will now be shown.

It is proved in the "Pear-shaped Figure" that the $\Pi(\gamma, \Delta_x)$ elliptic integral disappears from the expression for $\mathfrak{PQ}$ for all cases up to the third harmonics inclusive. I have also proved numerically that for the Jacobian ellipsoid the like is true for all the even zonal harmonics up to the tenth inclusive, and for the tesseral harmonics $i = 4$ $s = 2$ and $i = 4$, $s = 4$. It is thus certainly true in all cases used by me, and I do not care to spend perhaps much time in proving algebraically the general truth of the law.

The last two of our integrals will occur in the form

$$\int_0^\gamma \frac{\sin^4\psi}{\Delta_x^{\,4}\Delta}\,d\psi - B_x\int_0^\gamma \frac{\sin^2\psi}{\Delta_x^{\,2}\Delta}\,d\psi,$$

and I *assume* that the coefficient of $\Pi(\gamma, \Delta_x)$ in this expression always vanishes, as is *proved* to be true in all cases actually computed.

Hence

$$2B_x = \frac{1}{{q'_x}^2} - \frac{1}{q_x^2} + \frac{1}{\kappa^2 - q_x^2}.$$

Now the coefficient of F (γ) in this same combination of integrals is

$$\frac{1}{2q_x^2}\left[\frac{1}{q_x^2} - \frac{1}{{q'_x}^2} + 2B_x\right].$$

In this we may substitute for B_x its value, and thus find

$$\int_0^\gamma \frac{\sin^4\psi}{\Delta_x^4\Delta}\,d\psi - B_x\int_0^\gamma \frac{\sin^2\gamma}{\Delta_x^2\Delta}\,d\psi = \frac{1}{2q_x^2(\kappa^2-q_x^2)}\,\mathrm{F}(\gamma) - \frac{1}{2q_x^2{q'_x}^2(\kappa^2-q_x^2)}\,\mathrm{E}(\gamma) + \frac{\sin\gamma\cos\gamma\cos\beta}{2{q'_x}^2(\kappa^2-q_x^2)\,\Delta_x^2}.$$

This expression together with (1) give all the required integrals, and it only remains to tabulate f, g, h, A_x for the several types of function.

For the sake of brevity I write

$$C_x = (q_x^2-q_1^2)^2\,(q_x^2-q_2^2)^2\ldots(q_x^2-q_n^2)^2 \quad (x = 1,\,2\ldots n),$$

the factor which would vanish being in each case omitted.

When there is only one q, C_1 is to be interpreted as unity.

TABLE of Values of f, g, h, and A_x.

Type.	i order of harmonic.	s rank of harmonic.	f.	g.	h.	A_x.
EEC	$2n$	$2t$	∞	∞	∞	C_x
EES	$2n+2$	$2t$	$-\kappa'^2\prod_1^n(\kappa^2-q_x^2)^2$	$\kappa'^2\prod_1^n {q'_x}^4$	∞	${q'_x}^2(\kappa^2-q_x^2)\,C_x$
OOC	$2n+1$	$2t+1$	∞	$\prod_1^n {q'_x}^4$	∞	$-{q'_x}^2 C_x$
OOS	$2n+1$	$2t+1$	$\kappa'^2\prod_1^n(\kappa^2-q_x^2)^2$	∞	∞	$-(\kappa^2-q_x^2)\,C_x$
OEC	$2n+1$	$2t$	∞	∞	$\prod_1^n q_x^4$	$q_x^2 C_x$
OES	$2n+3$	$2t$	$-\kappa^2\kappa'^2\prod_1^n(\kappa^2-q_x^2)^2$	$\kappa'^2\prod_1^n {q'_x}^4$	$\kappa^2\prod_1^n q_x^4$	$q_x^2{q'_x}^2(\kappa^2-q_x^2)\,C_x$
EOC	$2n+2$	$2t+1$	∞	$\prod_1^n {q'_x}^4$	$-\prod_1^n q_x^4$	$-q_x^2{q'_x}^2 C_x$
EOS	$2n+2$	$2t+1$	$\kappa^2\prod_1^n(\kappa^2-q_x^2)^2$	∞	$-\kappa^2\prod_1^n q_x^4$	$-q_x^2(\kappa^2-q_x^2)\,C_x$

In all the types

$$B_x = 2\left[\frac{1}{q_x^2-q_1^2}+\frac{1}{q_x^2-q_2^2}+\ldots+\frac{1}{q_x^2-q_n^2}\right],$$

with the omission of the term which would be infinite.

We have generally $\mathfrak{B} = \frac{\mathfrak{A}}{\mathfrak{P}(\nu_0)}\frac{d}{d\nu_0}\mathfrak{P}(\nu_0)$. Hence by logarithmic differentiation of the expressions for the several types of $\mathfrak{P}$ we find results given in the following table :—

TABLE of the $\mathfrak{B}$ Integrals.

Type.	i order of harmonic.	s rank of harmonic.	$\mathfrak{B}_i^s \div 2 \sin \beta \mathfrak{A}_i^s$.
EEC	$2n$	$2t$	$\sum_1^n 1/\Delta_x^2$
EES	$2n+2$	$2t$	$\frac{1}{2}\sec^2\beta+\frac{1}{2}\sec^2\gamma+\sum_1^n 1/\Delta_x^2$
OOC	$2n+1$	$2t+1$	$\frac{1}{2}\sec^2\gamma+\sum_1^n 1/\Delta_x^2$
OOS	$2n+1$	$2t+1$	$\frac{1}{2}\sec^2\beta+\sum_1^n 1/\Delta_x^2$
OEC	$2n+1$	$2t$	$\frac{1}{2}+\sum_1^n 1/\Delta_x^2$
OES	$2n+3$	$2t$	$\frac{1}{2}+\frac{1}{2}\sec^2\beta+\frac{1}{2}\sec^2\gamma+\sum_1^n 1/\Delta_x^2$
EOC	$2n+2$	$2t+1$	$\frac{1}{2}+\frac{1}{2}\sec^2\gamma+\sum_1^n 1/\Delta_x^2$
EOS	$2n+2$	$2t+1$	$\frac{1}{2}+\frac{1}{2}\sec^2\beta+\sum_1^n 1/\Delta_x^2$

In the case of the zonal harmonics ($s = 0$), q_x/κ is always less than unity; for harmonics of rank 2 one of the q_x/κ is greater than unity and the rest are less; for rank 4 two of them are greater than unity and the rest less.

For the zonal harmonics there is some gain in simplicity by putting $\sin^2\theta_x = \frac{q_x^2}{\kappa^2}$. We then take the equation

$$\mathfrak{P}_{2n}(\mu) = a-b\cos^2\theta+c\cos^4\theta-\ldots = 0,$$

and find all the n roots, say $\theta_1, \theta_2\ldots\theta_n$.

If we solve the corresponding equation $\mathfrak{P}_{2n}{}^2(\mu) = 0$ for the tesseral harmonic of rank 2, we find one root for $\cos^2\theta$ to be negative. If this root corresponds to

θ_1, we must put $\cos^2\theta_1 = 1-\frac{q_1^2}{\kappa^2}$, so that $q_1^2 = \kappa^2[1+(-\cos^2\theta_1)]$. Similarly for the harmonics of rank 4, two roots correspond with imaginary angles, and so forth.

Subject to this explanation we may now regard the roots as defined by $\theta_1, \theta_2 \ldots \theta_n$.

Since $\Delta_x^2 = 1-q_x^2\sin^2\gamma$, we have $\Delta_x^2 = 1-\kappa^2\sin^2\gamma\sin^2\theta_x = 1-\sin^2\beta\sin^2\theta_x$, and $\mathfrak{P}_{2n}^{2t}(\mu) = \operatorname{cosec}^{2n}\gamma\,\Delta_1^2\Delta_2^2\ldots\Delta_n^2$.

If we write

$$D_x = (\sin^2\theta_x - \sin^2\theta_1)^2(\sin^2\theta_x - \sin^2\theta_2)^2\ldots(\sin^2\theta_x - \sin^2\theta_n)^2 \quad (n-1 \text{ factors}),$$

our former C_x may be written in the form $\kappa^{4n-4}D_x$, and the several coefficients in the expression for $\mathfrak{A}_i^s$ may be expressed as trigonometrical functions—some of which may, however, be hyperbolic.

We thus have

$$\begin{aligned}\mathfrak{A}_{2n}^{2t} = \frac{1}{2\kappa^{4n-1}}\prod_1^n(1-\sin^2\beta\sin^2\theta_x)^2\Bigg[\mathrm{F}(\gamma)\sum_1^n\frac{1}{D_x\sin^2\theta_x\cos^2\theta_x} \\ -\mathrm{E}(\gamma)\sum_1^n\frac{1}{D_x\sin^2\theta_x\cos^2\theta_x(1-\kappa^2\sin^2\theta_x)} \\ +\kappa^2\sin\gamma\cos\gamma\cos\beta\sum_1^n\frac{1}{D_x\cos^2\theta_x(1-\kappa^2\sin^2\theta_x)(1-\sin^2\beta\sin^2\theta_x)}\Bigg].\end{aligned}$$

This formula agrees with the result given for $\mathfrak{A}_2^s$ $(s = 0, 2)$ in § 4 of "The Pear-shaped Figure," although the formula is there expressed in terms of q^2, and $1/(\kappa^2-q^2)$ is replaced by its equivalent $(1-2q^2)/q^2q'^2$.

In the case of the even zonal harmonics of order i, all the θ's are real angles, and it facilitates the solution of the equation for θ to note that, with rough approximation (improving as the order of harmonic increases),

$$\theta_1 = \frac{\pi}{2i}, \quad \theta_2 = \frac{3\pi}{2i}, \quad \theta_3 = \frac{5\pi}{2i}, \ldots, \quad \theta_{\frac{1}{2}i} = \frac{(i-1)\pi}{2i}.$$

The following numerical values apply to the critical Jacobian ellipsoid :—

For the fourth harmonic $\theta_1 = 20^\circ\ 15'$, $\theta_2 = 61^\circ\ 11'$; the rough approximation gives 22° 30′ and 67° 30′.

For the sixth $\theta_1 = 14^\circ\ 1'{\cdot}9$, $\theta_2 = 42^\circ\ 12'{\cdot}2$, $\theta_3 = 71^\circ\ 8'{\cdot}6$; the rough approximation being 15°, 45°, 75°.

For the eighth $\theta_1 = 10^\circ\ 43'{\cdot}1$, $\theta_2 = 32^\circ\ 11'{\cdot}8$, $\theta_3 = 53^\circ\ 51'{\cdot}2$, $\theta_4 = 76^\circ\ 21'{\cdot}8$; the approximation being 11° 45′, 34° 15′, 56° 45′, 79° 15′.

For the tenth $\theta_1 = 8^\circ\ 40'$, $\theta_2 = 26^\circ\ 1'$, $\theta_3 = 43^\circ\ 26'$, $\theta_4 = 61^\circ\ 3'$, $\theta_5 = 79^\circ\ 28'$; the approximation being 9°, 27°, 45°, 63°, 81°.

The values of the several $\mathfrak{A}$'s found by quadratures were in every case too small;

the correct values are given in the table below. I find that for $\mathfrak{A}_4$ quadratures gave too small a value by a $\frac{1}{300}$th part; for $\mathfrak{A}_6$ by a $\frac{1}{140}$th part; for $\mathfrak{A}_8$ by an $\frac{1}{87}$th part.

The method which I have given above fails for the tenth zonal harmonic, unless we use logarithms of more than seven places; and it is not worth while to undertake so heavy a piece of computation. I conclude by extrapolation that for $\mathfrak{A}_{10}$ quadrature (carried out on exactly the same plan as in all the other cases) gives too small a result by a $\frac{1}{70}$th part of itself. I therefore augment in this case the result of the quadratures and find $\mathfrak{A}_{10} = 0{\cdot}11640$; this enables us also to compute $\mathfrak{B}_{10}$.

The following table gives the results of the whole computation[*]:—

TABLE of Logarithms of $\mathfrak{A}_i^s$ and $\mathfrak{B}_i^s$ Integrals.

i.	s.	$\log \mathfrak{A}_i^s + 10$.	$\log \mathfrak{B}_i^s$.
2	0	9·6931231	·0929494
2	2	9·3330037	·4066504
3	0	9·54617	·20462
4	0	9·4332383	·2657402
4	2	9·24250	·39502
4	4	9·04753	·43121
6	0	9·2701270	·3263106
6	2	9·14462	·39512
6	4	9·00632	·42458
8	0	9·15835	·35745
10	0	9·06595	·36897

§ 3. *Note on* § 15. "*The Determination of certain Integrals.*"

It has been found best to make some changes in this part of the work.

The integrals to be evaluated are denoted

$$ {}^{2p}\Lambda_{2m}^{\ 2n} = \int_0^{\frac{1}{2}\pi} \frac{\sin^{2p}\theta \cos^{2n}\theta}{\Delta_1^{\ 2m}\Delta}\, d\theta, $$

$$ \Omega_{2m}^{\ 2n} = \int_0^{\frac{1}{2}\pi} \frac{\sin^{2n}\phi}{\Gamma_1^{\ 2m}\Gamma}\, d\phi. $$

The integral ${}^{2p}\Lambda_{2m}^{\ 2n}$ may be made to depend on ${}^{0}\Lambda_{2m}^{\ 2n}$ (which is the same as $\Lambda_{2m}^{\ 2n}$ of the original paper), and therefore I only evaluate the latter.

These integrals were originally found as the differences of certain other functions, but it is not hard to give formulæ for finding them directly. I have done this and recomputed the whole series of values.[†]

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[*] The only error of any moment which I have found in my previous work is that in some of the cases I had forgotten to introduce the factor κ in some of the $\mathfrak{A}$'s after effecting the quadratures. The error in my results from this oversight was fortunately not serious.

[†] There is a misprint on p. 286. The function U_6^0 should be

$$ \frac{3\pi}{16\cos\beta\cos\gamma}\left[\sec^4\beta + \sec^4\gamma + \tfrac{2}{3}\sec^2\beta\sec^2\gamma\right]. $$

The series of values ${}^0\Lambda_0{}^{2n}$ were also computed independently from the series given on p. 537 of "Harmonics."

A little consideration will show that the differences of the series of functions ${}^0\Lambda_{2m}{}^{2n}$, with the signs of the odd differences changed, gives the series of functions ${}^{2p}\Lambda_{2m}{}^{2n}$. Stated analytically

$$(-)^r \Delta^r\, {}^0\Lambda_{2m}{}^{2p-2r} = {}^{2r}\Lambda_{2m}{}^{2p-2r}.$$

A table of the natural numbers ${}^0\Lambda_{2m}{}^{2n}$ is given, but the table of differences is not reproduced.

The following is the result of the recomputation :—

TABLE of the Λ Functions (Natural Numbers).

n.	${}^0\Lambda_0{}^n$.	${}^0\Lambda_2{}^n$.	${}^0\Lambda_4{}^n$.	${}^0\Lambda_6{}^n$.
0	2·7024906	8·034600	30·53878	132·38251
2	·9505345	1·4779482	2·866414	7·149917
4	·6559354	·8294118	1·1590804	1·8826818
6	·5285432	·6160958	·7537022	·9929042
8	·4543269	·5084364	·5844941	·6987687
10	·4044492	·4419004	·4909693	·5582507
12	·3680175	·3958484	·4306317	·4755180
14	·3399181	·3616261	·3878603	·4203234
16	·3173978	·3349328	·3556021	
18	·2988272	·3133708	·3295135	
20	·2831734			
22	·2697454			

TABLE of Logarithms of the Ω Functions.

n.	$\log \Omega_0{}^n$.	$\log \Omega_2{}^n$.	$\log \Omega^n{}_4$.	$\log \Omega_6{}^n$.
0	·2047610	1·0302912	1·8667641	2·7138144
2	9·8993673	·7715375	1·6492558	2·5319084
4	9·7729862	·6613000	1·5528790	2·4473549
6	9·6930884	·5897701	1·4886134	2·3893880
8	9·6346685	·5365117	1·4398970	2·3446714
10	9·5886267	·4939849	1·4005014	2·3080689
12	9·5506357	·4585472	1·3673618	2·2769972
14	9·5182995	·4281522	1·3387296	2·2499642
16	9·4901531	·4015325	1·3135070	
18	9·4652355	·3778480	1·2909612	
20	9·4428427	·3565096	1·2705764	
22	9·4226147			

The results in the original paper were not so accurate as I had thought they were. There was a mistake in the differences which give the Ω_6 series, affecting the values from $n = 10$ onwards, but as no use was made of the Ω_8 series as published, the mistake did not affect the final result.

§ 4. *Note on §§ 16, 17. The Integrals* σ_2, σ_4, ζ_4 *and* ω_i^s, ρ_i^s, ϕ_i^s.

An improvement has been made in the method of computing all these. The functions to be integrated were written in every case with a common factor $\operatorname{cosec}^2\gamma\,(\Delta_1^2-\Gamma_1^2)$; now this is equal to $\kappa^2\cos^2\theta+\kappa'^2\sin^2\phi$. In consequence of the substitution of this value for the common factor we are able to obtain the result as the sum of, instead of the difference between, two numbers. Another consequence is that we can dispense with the series of functions denoted Λ_{-2} and Ω_{-2}.

A single example of the way in which this change is applied will suffice. If we write

$$\left.\begin{aligned} f(\Lambda_{2n}{}^0) &= \alpha\,{}^0\Lambda_{2n}{}^0-\beta\,{}^0\Lambda_{2n}{}^2+\gamma\,{}^0\Lambda_{2n}{}^4-\delta\,{}^0\Lambda_{2n}{}^6 \\ f(\Lambda_{2n}{}^2) &= \alpha\,{}^0\Lambda_{2n}{}^2-\beta\,{}^0\Lambda_{2n}{}^4+\gamma\,{}^0\Lambda_{2n}{}^6-\delta\,{}^0\Lambda_{2n}{}^8 \end{aligned}\right\} n = 1,\ 2,$$

and denote by $f(\Omega_{2n}{}^0)$, $f(\Omega_{2n}{}^2)$, corresponding functions with α', β', γ', δ' for α, β, γ, δ and Ω in place of ${}^0\Lambda$; it is easy to show that

$$\begin{aligned}\sigma_2 = \frac{6}{\pi}\cos^2\beta\cos^2\gamma\,\{\kappa^2[f(\Lambda_2{}^2)f(\Omega_4{}^0)+f(\Lambda_4{}^2)f(\Omega_2{}^0)-Gf(\Lambda_2{}^2)f(\Omega_2{}^0)] \\ +\kappa'^2[f(\Lambda_2{}^0)f(\Omega_4{}^2)+f(\Lambda_4{}^0)f(\Omega_2{}^2)-Gf(\Lambda_2{}^0)f(\Omega_2{}^2)]\}.\end{aligned}$$

The computations as revised gave

$$\sigma_2 = \cdot 0136760, \qquad \zeta_4 = \cdot 000092343, \qquad \sigma_4 = \cdot 000176218.$$

Taking $\log\mathfrak{A}_3 = 9\cdot 5461687$, I found

$$\mathfrak{A}_3\left[\tfrac{1}{3}(\sigma_2)^2+2\zeta_4\right]-\tfrac{1}{3}\sigma_4 = -\cdot 00050051.$$

This differs by 4 in the seventh place of decimals from the old value.

In evaluating ω_i^s, ρ_i^s, ϕ_i^s when we use the form of $\mathfrak{P}_i^s$ involving f_0, f_2, f_4, &c., we have to put

$$[\mathfrak{P}_3(\mu)]^2 = F_0\sin^6\theta-F_2\sin^4\theta\cos^2\theta+\mathrm{F}_4\sin^2\theta\cos^2\theta,$$

and F_0, F_2, F_4 are easily found from α, β, γ, δ.

I then write

$$L_0 = f_0F_0, \quad L_2 = f_0F_2+f_2F_0, \quad L_4 = f_0F_4+f_2F_2+f_4F_0, \quad \text{\&c.},$$

and, when i denotes the order of the harmonic S_i^s concerned, write

$$f(\Lambda_{2n}{}^0) = L_0{}^{i+6}\Lambda_{2n}{}^0-L_2{}^{i+4}\Lambda_{2n}{}^2+L_4{}^{i+2}\Lambda_{2n}{}^4-\ldots(n = 1,\ 2),$$

$$f(\Lambda_{2n}{}^2) = L_0{}^{i+6}\Lambda_{2n}{}^2-L_2{}^{i+4}\Lambda_{2n}{}^4+L_4{}^{i+2}\Lambda_{2n}{}^6-\ldots(n = 1,\ 2).$$

These functions are then combined to give the required integrals.

A similar notation enables us to evaluate ϕ_i^s, which is given by

$$\phi_i^s = \frac{6}{\pi} \iint (\kappa^2 \cos^2\theta + \kappa'^2 \sin^2\phi) \frac{(S_i^s)^2}{\Delta\Gamma}\, d\theta\, d\phi,$$

so that

$$\phi_i^s = \frac{6}{\pi} \{\kappa^2 f(\Lambda_0^2) f(\Omega_0^0) + \kappa'^2 f(\Lambda_0^0) f(\Omega_0^2)\},$$

appropriate forms being attributed to $f(\Lambda)$, $f(\Omega)$.

The result of the procedure sketched is the following series of values, in which only the cases $i = 6$, $s = 2, 4$, are derived from approximate forms. For the sake of comparison I add the approximate values of ϕ_i^s as computed from the formulæ in "Harmonics." In the cases $i = 2$, $s = 0, 2$, the approximate results, derived from that paper, are multiplied by such factors as to make the approximate formulæ for $\mathfrak{P}_2(\mu)$ and $\mathfrak{C}_2(\phi)$ agree with the exact one when $\mu = 1$, $\phi = 45°$; and for $\mathfrak{P}_2^2(\mu)$ and $\mathfrak{C}_2^2(\phi)$ to make the coefficients of μ^2 and $\cos^2\phi$ agree with the exact formulæ.

TABLE of Logarithms of ω_i^s, ρ_i^s, ϕ_i^s.

i.	s.	$\log \omega_i^s + 10$.	$\log \rho_i^s + 10$.	$\log \phi_i^s$.	Approximate ϕ_i^s from formula in "Harmonics."
0	0	—	7·6310567	—	—
2	0	7·6714241	7·0286816	9·0051748 − 10	9·00518 − 10
2	2	(−) 5·6818162	(−) 5·0264000	7·0397377 − 10	7·03981 − 10
4	0	8·0332932	7·3558076	9·6886735 − 10	9·68861 − 10
4	2	(−) 8·25158	(−) 7·32157	1·72739	1·72729
4	4	8·30779	7·37092	3·81610	3·81612
6	0	7·96786	7·32449	9·69177 − 10	9·69303 − 10
6	2	(−) 8·72778	(−) 7·94094	—	2·20562
6	4	9·10094	8·13161	—	5·29999
8	0	7·78437	6·96857	9·75611 − 10	9·76872 − 10
10	0	(−) 7·9838	6·6024	9·8473 − 10	9·87800 − 10

Note that ω_{10} is negative while ϕ_{10} remains positive.

The calculation of the integrals for $i = 8$ and $i = 10$ was very laborious, and as the results tend to present themselves as the differences between large numbers, it is difficult to obtain accuracy with logarithms of only seven places of decimals. The integrals ϕ are much the most troublesome; indeed I do not claim close accuracy for ϕ_8; and as it appeared to be impossible to compute ϕ_{10} to nearer than 10 per cent. from the formula, I computed the several constituent integrals for the tenth harmonic by quadratures and combined them to find ϕ_{10}. The results derived from the approximate formulæ of "Harmonics" are given for the sake of comparison. They clearly give somewhat too large a value for the higher harmonics. I believe ω_{10} and ρ_{10} to be nearly correct.

If allowance be made for the difference of definition adopted in this paper from that used in "Harmonics" as regards the second zonal harmonic, it will be found that ω_2, ω_4, ω_6, ω_8, ω_{10}, when set out graphically, fall into an evenly flowing curve. The corresponding test for the ρ's is not quite so convincing, but there is nothing which implies a mistake. The values of ρ_0, ρ_2, ρ_4, ρ_6 fall well into line, and so do ρ_4, ρ_6, ρ_8, ρ_{10}, but there is a gentle elevation in the neighbourhood of ρ_6. In consequence of this slight waviness of the curve I recomputed the *whole* again independently, after it had been recomputed and verified once, and special attention was paid to ω_6 and ρ_6.

§ 5. *Final Synthesis of Numerical Results, and Conclusion.*

The several numerical values are combined just as in the original paper, but the numbers, of course, differ a little from those obtained before. The following table gives the final stage, inclusive of the additional terms now computed:—

i.	s.	(1) $[i, s]$.	(2) $(B_i^s)^2/C_i^s$.	(1) + (2).	B_i^s/C_i^s.
2	0	+ ·000138868	− ·000219736	− ·000080868	− ·12382
2	4	·000000717	+ ·000000970	+ ·000001687	− ·08056
4	0	·000092542	·000154732	·000247274	+ ·06273
4	2	·000001908	·000001190	·000003098	− ·000355
4	4	·000000012	·000000000	·000000012	+ ·0000017
6	0	·000031204	·000031146	·000062350	+ ·019564
6	2	·000003422	·000002107	·000005529	− ·000229
6	4	·000000014	·000000000	·000000014	+ ·0000003
8	0	+ ·000012905	·000006671	·000019576	+ ·007505
10	0	− ·000001030	+ ·000007358	+ ·000006328	− ·00667
			Sum =	·000265000	
			$\mathfrak{A}_3\left[\frac{1}{3}(\sigma_2)^2 + 2\zeta_4\right] - \frac{1}{3}\sigma_4$ =	− ·000500513	
			Numerator =	− ·000235513	

I then find $\log D = 9{\cdot}9840165$, $\log L = {\cdot}6454565$, $\log M = {\cdot}9591963$. From these we find $\mathfrak{c} = L\phi_2$, $\mathfrak{d} = M\phi_2^2$; whence

$\frac{B_2}{C_2}\mathfrak{c}$ =	− ·0553908
$\frac{B_2^2}{C_2^2}\mathfrak{d}$ =	·0008037
$\mathfrak{b}$ =	·0316007
Denominator =	− ·0229864

The Numerator divided by the Denominator is $-\delta\omega^2/4\pi\rho e^2$, whence

$$\log \frac{\delta\omega^2}{4\pi\rho e^2} = (-)\, 8{\cdot}01054.$$

With $\dfrac{\omega^2}{2\pi\rho} = {\cdot}141990$, from § 7 of the "Pear-shaped Figure," we have

$$\omega^2 + \delta\omega^2 = \omega^2[1 - {\cdot}1443066e^2].$$

Thence we find

$$f_2 = {\cdot}195979e^2, \quad f_2^2 = {\cdot}603177e^2.$$

These values differ sensibly from the old ones.

The moment of inertia with $\log \mathrm{a} = 9{\cdot}8559759$ is given by

$$A_j - A_r = \frac{3M\mathrm{a}}{2\pi\rho k_0}[1 + {\cdot}157786e^2].$$

The moment of momentum is

$$\frac{3M^2\mathrm{a}\omega}{2\pi\rho k_0}[1 + {\cdot}085633e^2].$$

As before, we find the pear-shaped figure to be stable, because the moment of momentum is greater than that of the critical Jacobian, provided that the infinite series does not amount to too great a sum.

If ϵ be the uncomputed residue of $\Sigma\left\{[i, s] + \dfrac{(B_i^s)^2}{C_i^s}\right\}$, I then find, as before, that the moment of momentum is

$$\frac{3M^2\mathrm{a}\omega}{2\pi\rho k_0}[1 + {\cdot}085633e^2 - 499{\cdot}586\epsilon e^2].$$

The coefficient of e^2 will be positive and the pear stable, provided that

$$499{\cdot}586\epsilon < {\cdot}085633,$$

or

$$\epsilon < {\cdot}0001714.$$

The eighth zonal harmonic gave a contribution of ·0000196, and the tenth of ·0000063. These are respectively a ninth and a twenty-seventh of the critical total. The pear is then stable unless the residue of the apparently highly convergent series shall amount to more than 27 times the value of the last term computed. M. Liapounoff claims in effect to prove that this is the case, but to me it seems incredible. I look for the discrepancy between our conclusions in some other direction.

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[PLATES 1–2.]

THE THERMOMAGNETIC ANALYSIS OF METEORIC AND ARTIFICIAL NICKEL-IRON ALLOYS

BY

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II. *The Thermomagnetic Analysis of Meteoric and Artificial Nickel-iron Alloys.*

By S. W. J. Smith, *M.A., A.R.C.S., Royal College of Science, London.*

Communicated by Sir Arthur W. Rücker, *F.R.S.*

Received November 1, 1906,—Read February 14, 1907.

[Plates 1–2.]

Contents.

SECTION I.—DESCRIPTION OF THE MATERIALS OF WHICH THE THERMOMAGNETIC PROPERTIES WERE INVESTIGATED.

§ 1. THE experiments described in this paper arose from the desire of Sir ARTHUR W. RÜCKER to obtain, in connection with his researches on the nature of the Earth's magnetic field, further data concerning the properties of such magnetic materials of natural origin as may be present in appreciable quantity in the Earth's crust.

Iron of cosmic origin contains nearly always an appreciable quantity of nickel, and the magnetic properties of this material, especially their variation with temperature, have received very little attention. Most of the published data are qualitative only, and from them no very definite conclusion can be drawn beyond the fact that meteoric iron appears to be of very variable permeability. It was, therefore, thought desirable to make a careful quantitative study of a typical example of such material.

§ 2. The meteoric iron used in the experiments was bought from the firm of Dr. A. E. FOOTE, and the mass from which the sample was cut is described by A. E. FOOTE in the 'American Journal of Science' [4], vol. 3, p. 65, 1897. The whole meteorite weighed about 237 kilogs. and was found in the Sacramento Mountains, Eddy Co., New Mexico. A careful analysis of some fragments yielded the results :—

$$\begin{aligned} \text{Fe} &= 91{\cdot}39 \\ \text{Ni} &= 7{\cdot}86 \\ \text{Co} &= 0{\cdot}52 \\ \hline & \ 99{\cdot}77 \end{aligned}$$

The material is thus apparently remarkably free from elements other than those of the ferromagnetic group.

After a ring about 2 centims. deep and 5½ centims. external diameter had been cut from the sample supplied, a solid disc-shaped core, about 3¾ centims. in diameter, remained. The ends and cylindrical surface of this were afterwards polished carefully and etched. At the conclusion of the experiments, the outer oxidised layer of the ring was removed on the lathe and the ring was then etched in order that its structure might be compared with that of the material which had not received thermal treatment.

§ 3. Different samples of the turnings produced during the formation of the ring were kindly analysed by Mr. E. A. WRAIGHT, of the Royal School of Mines, with the following mean result:—

Fe = 92·84 (92·5 to 93·0 in different samples)
Ni = 6·81
Co = 0·37.

In some of the samples there were traces of chromium, whilst others contained up to 0·025 per cent. of sulphur. Examination of the polished surface of the core above mentioned showed the presence of an isolated speck of a brass-coloured mineral which was almost certainly sulphide of iron (troilite), and it is probable that the sulphur found in some analyses was present in this form. No trace of carbon or phosphorus was found in the analyses.

§ 4. Mr. A. FOWLER, Assistant Professor of Physics in the Royal College of Science, kindly examined the meteorite spectroscopically between the D lines and λ 4170 and found that there were no lines not accounted for by Fe, Ni, Co and Cr. The cobalt lines were relatively inconspicuous. Three chromium lines were identified with certainty.

§ 5. The grosser structure of the meteorite was shown very clearly by the markings on the polished and etched cylindrical core. The distribution of the more and less nickeliferous layers was easily discernible. The actual thicknesses of the layers, and their geometrical arrangement with respect to one another, could be observed by tracing the course of individual layers across the plane and cylindrical surfaces of the core. The approximate relation between the positions of the layers observed is represented in fig. 1.

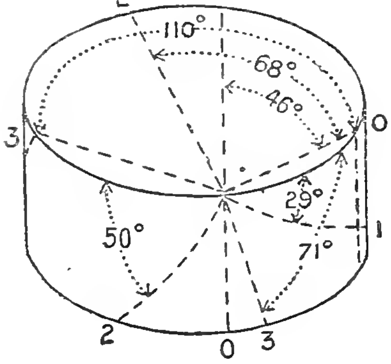


Fig. 1.

All the layers observable were parallel to one or other of the four planes represented by their traces upon the plane and cylindrical surfaces, viz., 00, 11, 22 and 33 respectively. Some of the layers appeared to be appreciably curved. The numbers marked on the plane circular face in fig. 1 were judged to be the closest approximations that could be got to the general directions of the layers.

The true angles between each of the planes 00, 11, &c., and the plane faces of the core were determined by means of a hand goniometer. The numbers on the cylindrical surface in the diagram represent these angles.

Within the limits of observation the plane 00 was at right angles to the plane faces of the core. This accidental circumstance has the effect of simplifying slightly the calculation of the angles between the various planes. For, taking the plane of the circular face of the core as the plane of xy, the plane 00 may be taken as the plane of yz. Attention being paid to signs, the intercepts of each of the other three planes on the axes of x, y and z are then in the ratio

$$\tan\theta : 1 : \sin\theta \tan\phi,$$

where θ is the angle between the trace of 00 and of one of the other planes on the circular face and ϕ is the real angle between the latter plane and the circular face. Hence, using the data given on the diagram, the direction-cosines of the planes 11, 22 and 33 can be calculated.

In this way the angles between the planes of the layers were found to be :—

$$\theta_{01} = 70^\circ,\ \theta_{12} = 77^\circ,\ \theta_{23} = 71^\circ,\ \theta_{30} = 71^\circ,\ \theta_{02} = 73^\circ,\ \theta_{13} = 61^\circ.$$

Hence it is seen that, with the exception of 11, the planes are inclined to one another in practically the same way as the faces of a regular octahedron, the interfacial angle for the latter being 70° 32′ approximately.

The markings on the plane faces of the cylindrical core, from which the measurements were taken, are shown in the accompanying photographs, figs. 2 and 3 (Plate 1), which are slightly less than natural size (actual diameter of core about 3·7 centims.). The relative position of the markings in space would be reproduced by rotating either of the photographs through 180° about the line 00 and then placing it behind, and about 1·8 centims. away from, the other photograph. The markings on the cylindrical part of the surface of the core are very distinct, but difficult to reproduce photographically owing to the curvature. On this part of the surface, the layers parallel to 11, which are not very clearly seen on the flat ends (see photographs), are very numerous, owing to the acuteness of the angle (29°) which these layers make with the flat ends, and are as conspicuous as the layers running in the other directions.

Since the layers parallel to 00 run practically perpendicular to the plane ends of the core, the true thicknesses of these layers are represented in the photographs. On the other hand, the thicknesses of the layers parallel to 11 are about one-half (= sin 29°) of the apparent thicknesses shown in the photographs. The thickness of a layer parallel to 22 is about three-quarters (= sin 50°) of the apparent thickness, whilst the layers parallel to 33 are about 5 per cent. thinner than they appear in the photographs. From these data it will be seen that the distribution of the layers is even more regular than appears from the photographs. At the same time, the want of symmetry in the numbers given, showing an apparent anomaly in the positions of the layers parallel to 11, is, I think, too great to be accounted for as arising from unavoidable errors of observation.

The chief importance, for the present purpose, of the numbers and description just given lies in the fact that they serve to define the geometrical distribution of the alloys of different composition in the ring of which the permeability was examined. It was proved directly by polishing and etching the ring at the conclusion of the experiments that the regularity of distribution observed in the core extended to the portion of the material of which the ring was composed.

§ 6. The micro-structure of the meteorite is shown in the four photographs (Plate 2), for three of which I am indebted to Mr. WRAIGHT.

The photographs *a* and *b* represent different portions of the etched surface magnified about 50 diameters. The duller portion of the surface (crossed by sets of fine parallel "Neumann" lines) is in each case the easily etched constituent "kamacite." The brighter less easily etched constituent is "taenite." In the photograph *a* the thin bands of taenite are almost rectilinear, and there are numerous subsidiary, discontinuous bands. The centre of fig. *b* shows that there is sometimes no taenite between contiguous layers of kamacite. Lower in the figure there is an unbroken band of taenite separating two layers of kamacite, while in the upper part of the figure more nickeliferous material occurs in the gaps between layers of kamacite. Fig. *c* shows a portion of the surface magnified about 80 times. It suggests, like *b*, that the crystallisation of the taenite is subsequent to that of the kamacite, and also that the former is not in reality homogeneous, since the comparatively thick band of taenite in the middle of the figure has obviously been unequally etched by the reagent (*cf.* COHEN, "Meteoritenkunde," I., p. 80 *et seq.*). Similar inequalities of etching are shown in the lower band of taenite in the negative from which fig. *b* was obtained.

In obtaining these three photographs the degree of etching was very slight—the minimum amount necessary to bring out the structure represented.

In the photograph *d* (magnification roughly 500 diameters), which I took later, the degree of etching was much greater. The surface of the meteorite was no longer approximately plane, and the different parts could not be simultaneously focussed. The dark parts of the field are the deeply etched and unfocussed kamacite. The regions partly dark and partly bright represent highly magnified portions of the bands of etched taenite, in one of which there are distinct traces of lamination.

§ 7. The nickel-iron alloy, of which the magnetic properties were compared with those of the meteorite, was kindly supplied to me by Mr. R. A. HADFIELD, M.Inst.C.E., and was a sample of the 5·81 per cent. nickel steel described by him in the 'Proceedings, Institute Civil Engineers,' vol. 138, p. 114, 1899, where its composition is given as follows :—

Ni = 5·81
C = 0·18
Si = 0·31
S = ...
P = ...
Mn = 0·65
Fe (by difference) = 93·05.

The ring was forged from the rod supplied and turned down until its dimensions were nearly the same as those of the meteoric ring.

The dimensions of the rings, before winding for the permeability measurements, were as follows :—

Ring.	External diameter.	Internal diameter.	Axial depth.
	centims.	centims.	centims.
Meteoric iron . . .	5·40	4·37	1·89
Nickel steel . . .	5·41	4·37	1·90

SECTION II.—PRELIMINARY MEASUREMENTS OF PERMEABILITY AT THE AIR TEMPERATURE.

§ 1. The determination of the permeability of the meteoric iron in its original state as received was made in the ordinary way by the ballistic method. The ring, of the dimensions given above, was wound with a primary and secondary of copper wire, each silk-covered and further insulated by a coating of shellac varnish. The inductive effects obtained from the ring were compared with those obtained from a standard inductor.

§ 2. The following numbers represent values obtained at a temperature of 19° C. for corresponding values of μ and H and of B and H when the values of the latter were taken through a cycle.

H.	B.	μ.	H.	B.	μ.
In C.G.S. units.			In C.G.S. units.		
0·089	9·16	103·2	−0·261	−30·03	—
0·175	19·26	110·3	−0·346	−42·57	—
0·261	29·63	113·7	−0·261	−35·15	—
0·346	41·08	118·8	−0·176	−26·95	—
0·261	33·40	—	−0·089	−17·51	—
0·176	25·19	—	0·0	− 7·68	—
0·089	15·63	—	0·089	3·91	—
0·0	5·25	—	0·176	15·22	—
−0·089	− 6·06	—	0·261	28·02	—
−0·176	−17·51	—	0·344	40·54	—

It is well known that for pure iron and for many iron alloys the values of μ and H in weak fields are connected by a linear relation of the form

$$\mu = a+b\mathrm{H},$$

where a and b are constants.

Assuming that this relation may hold in the present case and calculating from the numbers just given, by the method of least squares, the most probable values of a and b, we find

$$\mu = 99{\cdot}5+55{\cdot}2\mathrm{H}.$$

The following table shows how far the values of μ calculated from this equation agree with those actually found.

Observed.	Calculated.
103·2	104·4
110·3	109·1
113·7	113·9
118·8	118·5

It will be seen that the agreement between corresponding numbers is within about 1 per cent.

§ 3. The values of μ and H given above were deduced from the observations in the ordinary way by assuming that the intensity of the field in the ring (for a given current in the primary) was uniform and equal to that at the mean radius.

The assumption that μ is constant throughout the cross-section of the ring, and that H has the value corresponding to the field intensity at the mean radius is, of course, very nearly true when the radial width of the ring is small compared with the mean radius. But if this latter condition is not fulfilled, or if the permeability varies rapidly with the field, the error introduced by this method of calculation may be considerable.

Although the dimensions of the ring were such that the intensity of the magnetising field for a given current in the primary coil would be more than 20 per cent. greater at the inner than at the outer surface of the ring, it was thought, having regard to the nature of the material examined, that the ordinary method of calculation would probably be as appropriate as any other, and that the degree of concordance of the numbers already given was sufficient for the purpose in view. Nevertheless, it is of interest to notice that, if the relation $\mu = a+b\mathrm{H}$ is approximately true, a close approximation to strictly corresponding values of μ and H can be easily obtained, even when the ratio of the radial width to the mean radius is considerable, or when the variation of μ with H is large. The inductive effect per turn of the ring secondary is $\int \mathrm{B}\,ds = \int \mu\mathrm{H}\,ds$, where ds represents an element of the cross-section of the ring, H is the intensity of the field at this element, and μ is the value of the permeability corresponding to H. Hence, assuming the linear relation between μ and H, stated above, we get

$$\int \mu \mathrm{H}\, ds = a\int \mathrm{H}\, ds + b\int \mathrm{H}^2\, ds,$$

from which it follows at once that $\int \mu\mathrm{H}\,ds/\int \mathrm{H}\,ds$, being equal to $a+b\int \mathrm{H}^2\,ds/\int \mathrm{H}\,ds$, represents the permeability of the material for a field of intensity $\int \mathrm{H}^2\,ds/\int \mathrm{H}\,ds$.

The value of $\int \mu\mathrm{H}\,ds$ is determined directly by experiment, and the values of $\int \mathrm{H}^2\,ds$ and of $\int \mathrm{H}\,ds$ can be calculated from the constants, geometrical and electrical, of the ring.

In the present case, the ring being nearly rectangular in cross-section, it was found that if μ_m and H_m represent strictly corresponding values of permeability and field, while μ and H represent approximately corresponding values as calculated in the ordinary way, then

$$\mu_m = \cdot 996\mu \quad \text{and} \quad \mathrm{H}_m = 1\cdot 006\mathrm{H}.$$

That is, values of μ and H calculated in the ordinary way would require to be reduced 0·4 per cent. and increased 0·6 per cent., respectively, in order to give the true corresponding values of permeability and field intensity.

The cross-section of the ring is frequently a rectangle terminated by semicircles, and we can then suppose the ring to be made up of a circular and a rectangular part. To complete the calculation in this case, according to the method just described, it is necessary to find the expressions for μ and H in the case of a ring of circular cross-section.

This is easily accomplished, since, as will be seen, in this case

$$\int \mathrm{H}\, ds = 4\pi \mathrm{N} i \{r_2 - \sqrt{r_2^2 - r_1^2}\}$$

and

$$\int \mathrm{H}^2\, ds = 8\pi \mathrm{N}^2 i^2 \{(r_2/\sqrt{r_2^2 - r_1^2}) - 1\},$$

where r_1 is the radius of the circular cross-section, r_2 is the mean radius of the ring, and N and i are the number of turns and the current, respectively, in the ring primary.

It may be noticed that the method of calculating corresponding values of μ and H, just described, would probably always give more accurate values than the ordinary method, even if the relation between μ and H, over a considerable range, were only expressible in the form

$$\mu = a + b\mathrm{H} + c\mathrm{H}^2 + \ldots,$$

for in many cases the assumption, that within the limits of H experienced in the ring a linear relation between μ and H is fulfilled, would not lead to appreciable error. All the values of permeability given later have been calculated according to this method.

§ 4. There is a further source of inaccuracy in the ordinary method of measuring permeability, of which the effects are usually small, but can on occasion become quite noticeable. It may be of interest to describe a method of procedure by which such effects can be eliminated almost entirely.

In the usual way of measuring permeability by the ballistic method the galvanometer circuit includes, in addition to the ring secondary, one of the two coils of an inductor not containing iron. The convenience of this arrangement arises from the fact that by its use measurements of resistance are avoided which otherwise would be necessary owing to the fact that the total flow of electricity in a circuit, in which a given change of induction is produced, depends upon its resistance. The method is especially convenient when, as in experiments of the kind described in this paper, the resistance of the secondary circuit has a succession of different values. But, unless certain precautions are taken, values of the permeability determined in the way just indicated are frequently liable to quite appreciable error owing to the effect of hysteresis in the ring secondary.

The quantity of electricity indicated by the galvanometer throw, when a current is established in the primary either of the inductor or of the ring, is a measure of the total change of induction in the secondary circuit. When a current is established in the primary coil of the ring the total change of induction in the secondary of the inductor is zero and the galvanometer throw therefore indicates the total change of induction in the ring secondary. But when a current is established in the primary of the inductor, the resulting total change of induction in the secondary circuit, indicated by the galvanometer throw, does not strictly represent the change of induction in the secondary of the inductor alone, because, owing to hysteresis, the total change of induction in the ring secondary is not zero. The induced current in the secondary, rising from zero to a maximum value and then again falling to zero, causes the iron in the ring to be subject to a magnetic force varying in the same way. In consequence the iron is left magnetised and the total quantity of electricity which circulates in the secondary circuit is less than would have been the case if there had been no hysteresis by an amount depending on the particular sample of iron and upon the magnitude of the changing field to which it is subjected in the way described.

The following numbers will serve to show the relative importance of the effect in question in the case of the experiments herein described. The meteoric iron ring was demagnetised by the method of continued reversal and diminution, and a current was then established in the primary of the inductor. This caused a galvanometer throw of 6·35 centims. The current was then broken and a deflection of 6·25 centims. was obtained in the reverse direction. The current was then again made and broken, and the respective throws were 6·3 centims. and 6·25 centims. The whole process was then repeated and the observed throws were 6·35, 6·15, 6·25 and 6·25 centims. The ring secondary was next cut out of the circuit and replaced by an exactly equal secondary containing no iron. On now making or breaking the current in the inductor primary the galvanometer throw was 6·43 centims.

The artificial nickel-iron ring showed a similar behaviour, but the differences between the various throws were much smaller than in the case of the meteoric iron, just as the observed hysteresis effect was much less.

The interpretation of these results is, of course, simple. The throw was greatest when the ring secondary was replaced by an equal resistance containing no iron because of the absence of hysteresis. This throw is that required for the correct calculation, in the usual way, of the value of the induction in the iron from which the permeability is deduced. The throw obtained on first completing the inductor primary circuit, after demagnetisation of the iron ring, was greater than the subsequent throws, which were practically equal, for a reason which is immediately obvious on consideration of the form of the curve showing the change of induction in an iron ring when subjected to a cyclic field.

Assuming the ring to be demagnetised, the effect of the transient current in its secondary when the inductor primary circuit is established is to change the induction in the iron in the way represented by the curves Ob_1, b_1b_2. The final induction in the ring secondary is indicated by Ob_2 and the magnitude of this ordinate is a measure of the difference between the first throw after demagnetisation and that obtained from a similar circuit containing no iron. When the current in the inductor primary is broken, the induction in the ring secondary changes in a way represented by $b_2b_3b_4$, and the line b_2b_4 represents the total change of induction in the ring secondary during the second step. Similarly b_4b_2 represents, approximately, the total change of induction when the inductor primary circuit is again completed, and so on. The length of b_2b_4 being approximately double that of Ob_2, the effect of hysteresis is more pronounced in the second and succeeding throws than in that first observed after demagnetisation.

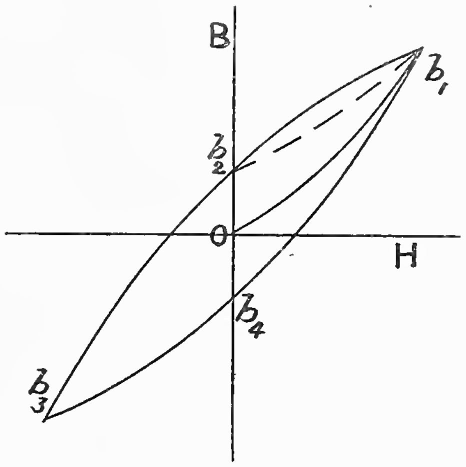


Fig. 6.

Assuming this to be the correct interpretation of the results, there follows at once a method of eliminating the effect of hysteresis directly without substituting for the ring secondary an equivalent resistance not containing iron. Suppose that, after demagnetising, the inductor primary circuit is completed. This causes a galvanometer throw which need not be recorded and leaves the induction in the ring secondary in the state represented by Ob_2. Now open the secondary circuit and then open the inductor primary circuit. Now close the secondary circuit again. The induction in the ring secondary will still be represented by Ob_2. Finally complete the inductor primary circuit again and observe the galvanometer throw. This throw will correspond truly with the change of induction in the inductor secondary and will be free from the effect of hysteresis in the secondary of the ring. This follows because the total induction in the ring secondary will be practically the same when the transient current has ceased as it was before the inductor primary circuit was completed for the second time. The induction in the ring will have changed in the way represented by the dotted curve b_2b_1 and by the full curve b_1b_2, *i.e.* its value at the end will be practically the same as at the beginning, viz., Ob_2.

This argument was verified by direct observation. The throw obtained by the method just described was indistinguishable from that obtained on replacing the ring secondary by an equivalent resistance not containing iron.

§ 5. The possible effects of external fields, constant or variable, existing during the measurements remain to be considered.

(*a*) The majority of the permeability measurements described were made while using magnetising fields comparable with that of the Earth, and it might seem that the observations could be influenced appreciably by the presence of the latter field.

Assuming the ring to be placed with its axis of figure in the direction of the Earth's field, it is of course seen at once that the effect of the external axial magnetising force upon the magnetic state of the ring is greatly diminished, owing to the shortness of the ring in the direction of its axis, by the demagnetising force which results from the magnetisation of the ring by the field. But it might be expected that if this axial field were such that it produced an intensity H_a within the ring, appreciable in magnitude compared with the intensity H of the magnetising field due to the ring primary, its presence would materially affect the amount of induction observed on establishing the field H.

(*b*) Another source of possible error, more likely to be serious in the measurements at the higher temperatures, was the field due to the current in the coil by which the ring was heated. Thus, to take a particular case, the current in the ring primary for permeability measurements was about 0·16 ampère; whilst in the bifilarly wound heating coil surrounding the ring a current of more than 2 ampères was required in order to keep the temperature of the ring at 700° C. It might seem therefore that if the bifilarity were not perfect, the permeability measurements, with a field corresponding to 0·16 ampère, taken at ordinary temperatures, would not be exactly comparable with those taken at high temperatures under the influence of the same primary field.

It was impossible of course to make the bifilarity perfect in practice. The following numbers, obtained by means of a ring wound as described later, serve to show the degree of approximation to bifilarity attained. A current of 0·23 ampère in the ring primary gave an inductive throw of 25·0 centims. of the galvanometer in the secondary circuit. A current of 0·66 ampère in the heating coil gave a throw of 0·48 centim. Hence the ratio of the fields produced by the same current in the primary and in the heating coil respectively would be approximately 150 : 1. Thus, assuming proportionality between induction throws and corresponding fields, the field due to the heating coil when the steady current was 2 ampères would be roughly $\frac{1}{15}$ of that used in the permeability observations.

§ 6. To find how far effects arising from either of the causes enumerated above were likely to influence the measurements, subsidiary experiments were made upon a wrought-iron ring of the same dimensions as the meteoric ring. These experiments showed that neither the influence of the Earth's field nor want of bifilarity in the heating coil would produce appreciable effect upon the form of the temperature-permeability curves, for a constant field, determined in the way described in the paper. A primary, a secondary, and a tertiary—the latter to represent a unifilar heating coil—were wound upon the wrought-iron ring. The ring was then placed at the centre of a large solenoid, so that its axis of figure coincided with the axis of the solenoid. By means of this "axial solenoid" a field of any desired magnitude could be produced in the direction of the axis of the ring.

The ring was taken through a succession of cycles under different conditions of steady current in the axial solenoid and in the tertiary coil. The demagnetisation of the ring previous to the determination of each cycle was performed in the ordinary way by the method of continuous reversal and diminution of a current in the ring primary.

The ordinary permeability-hysteresis cycle, with no current in the axial solenoid or in the ring tertiary, was first obtained. Cycles were then performed with currents of different magnitude in the axial solenoid. The axial field with the greatest current used was about 25 C.G.S. units. It was found that if this field was established *before* the demagnetisation process was performed, the permeability and hysteresis curves subsequently obtained were practically identical (for both directions of the axial solenoid field) with those of the "ordinary cycle." It was only when the axial field was established *after* demagnetisation that a perceptible difference in the forms of the curves could be noted.

Similar results were obtained with a steady current in the tertiary coil, the current in the axial solenoid being zero, and also with the axial solenoid and tertiary fields acting simultaneously.

SECTION III.—ARRANGEMENT OF THE APPARATUS FOR MEASUREMENTS OF PERMEABILITY OVER A WIDE RANGE OF TEMPERATURES.

§ 1. The method of carrying out the permeability measurements over a wide range of temperatures differed little from well-known methods, and needs only a very brief description. The current in the heating circuit was observed by means of a Weston ammeter reading to 5 ampères, and was derived from the main supply—of which the voltage (continuous) was about 100; it was regulated by means of incandescent lamps, of variable number, arranged in parallel, and by bare wire resistance boards of the ordinary type. The resistances of the ring secondary and primary were measured by means of a previously calibrated Callendar and Griffiths bridge. The demagnetisation circuit contained a shunted voltmeter similar to that used in the primary circuit (see below), and the current strength was varied by means of wire resistances and a zinc sulphate trough. The inductive effects in the secondary circuit were measured by the apparatus already mentioned in connection with the preliminary experiments. The primary currents were measured by a Weston voltmeter (reading to 5 volts) shunted by a resistance of 10 ohms, which was not heated appreciably by the currents traversing it. It was found, by calibration, that a deflection of 50 scale divisions on the voltmeter (30 divisions = 1 volt) corresponded very nearly to a current of 0·017 C.G.S. units in the primary circuit. The adjustment of the primary current to a constant value at different temperatures, notwithstanding variation in the resistance of the ring primary owing to temperature change, was accomplished by means of resistance boxes, and a stretched wire of variable length included in the primary circuit.

§ 2. The temperature of the ring at the time of each observation of permeability was deduced from the resistance of the secondary. The method of deduction was to assume the relation

$$R_\theta = R_0 (1 + a\theta - b\theta^2)$$

between the resistance of the ring secondary and its temperature. The values of a and b were determined, in the case of the meteoric iron, by constructing a platinum thermometer out of wire taken from the same reel as the secondary, and in the other cases by constructing a thermometer out of the secondary coil itself, re-wound for that purpose. In each case the resistances of the thermometer at the freezing- and boiling-points of water, and at the boiling-point of sulphur, were taken in the usual way, a previously calibrated bridge being used for the purpose.

Each of the three platinum thermometer observations, with each of the wires used, of corresponding values of temperature and resistance, was estimated to be measured correctly within 0·1 per cent. With this degree of accuracy the probable error in the estimation of a was about 1 per cent., and in the estimation of b about 15 per cent. The error in the estimation of a temperature of 700° C. would, under these circumstances, amount to about 5° C. The values of the higher temperatures given in the subsequent tables may therefore be regarded as subject to an error certainly less than 10° C.

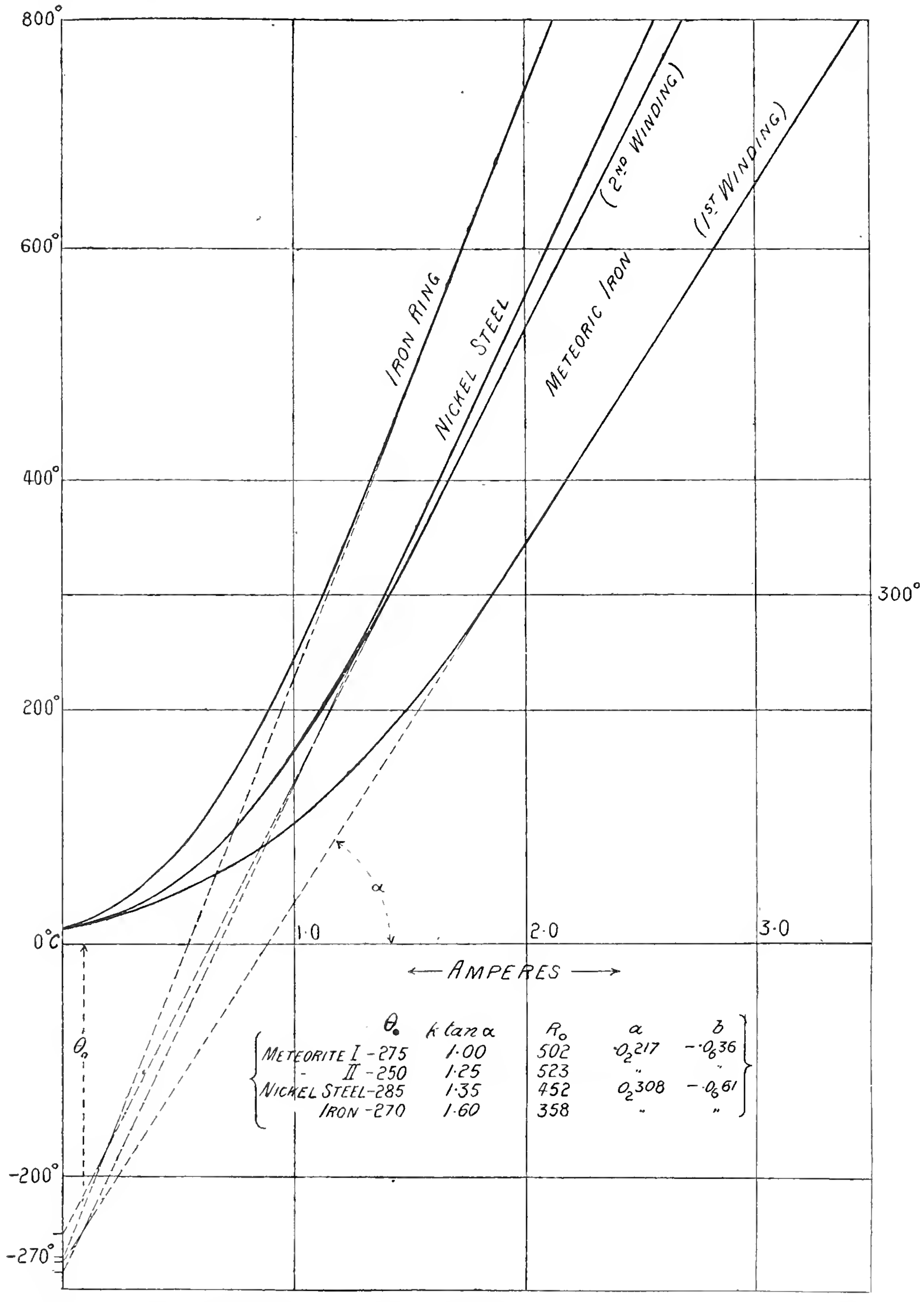
§ 3. In the first experiments the heating coil was placed between the primary and secondary coils, but in the later experiments the heating coil was wound outside the other two. The method of winding was as follows :—Two strips of mica were cut of such size that one could be bent into the form of a hollow cylinder fitting inside the ring, and the other into a cylinder fitting outside. The depth of these cylinders was slightly greater than that of the ring, and equidistant notches were made along each edge of the two cylinders. The distance between consecutive notches in each edge was proportional to the circumference of each cylinder, and their number was equal to the number of turns of wire it was proposed to wind round the ring. Two annuli of mica were next cut of such size as to fit closely between the mica cylinders. The cylinders and annuli were then fitted over the ring and were kept in position finally by the windings of platinum wire which enveloped them. The second and third coils were wound in the same way as the first. The terminals of each coil were brought out through holes pierced in one of the annuli serving for the winding and insulation of the coil wound over it. In this way it was found to be easy, after practice, to wind the permeability coils and the heating coil fairly uniformly and with very perfect insulation from one another—nothing but mica being used in the insulation. In the earlier experiments, layers of thin asbestos ribbon were wound between each mica insulation, partly because under these circumstances it was easier to keep the mica of the next coil in position during the winding of that coil, and partly to diminish the possibility of short-circuiting between consecutive coils. The winding of the coils being completed, the ring was placed upon a sheet of mica through which holes for the passage of the terminals of the coils were pierced. This sheet of mica was then laid on a small wire tripod, which rested on a block of hard wood about 5 centims. thick. This block of wood was also supported on a tripod, and thick insulated copper leads projected through it vertically below the ring. The outer ends of these leads were provided with binding screws, while the inner end of each was connected to a coil terminal. (There were altogether eight of these leads, six for the coil terminals and two for the short platinum loop used for compensation when determining the temperature of the ring secondary by measuring its resistance.)

A large inverted beaker was placed on the top of the block of wood, and rested in a deep circular groove about half-filled with mercury. By this means the ring, which was nearly at the centre of the beaker, was kept out of contact with the outside air. There were, however, two glass tubes, leading from outside into the beaker through the wooden base, by means of which the air within the beaker could be withdrawn and replaced by dry air or other gas. The beaker was kept in a fixed position with respect to the baseboard by an asbestos disc placed above it and attached by wires to the board.

A rectangular cover of asbestos board was fitted on the top of the wooden baseboard, and by this means a layer of air about 5 centims. thick was enclosed between the beaker and the outer atmosphere. In most of the experiments a smaller asbestos box was placed inside the beaker and enveloped the ring.

§ 4. In this apparatus, with a given current in the heating coil, the temperature usually became practically constant in less than an hour, but in most cases the permeability measurements were not taken until about two hours after the heating was begun.

The relation between the steady temperature in the apparatus and the current required to produce it is interesting. It is shown for each of four series of experiments in fig. 7.



	θ_0	$k \tan \alpha$	R_0	a	b
METEORITE I	-275	1·00	502	$\cdot 0_2 217$	$-\cdot 0_6 36$
" II	-250	1·25	523	"	"
NICKEL STEEL	-285	1·35	452	$0_2 308$	$-\cdot 0_6 61$
IRON	-270	1·60	358	"	"

Fig. 7. Curves showing relation between heating current and temperature for each ring.

The conditions under which the heating took place differed appreciably in the different series. For example, in the experiments with meteoric iron (first winding) there was no asbestos box surrounding the ring within the beaker, and the heating coil was between the other two. But in every case, for temperatures above 300° C. and below 800° C., the relation between temperature and current is almost exactly linear and can be expressed as

$$(\theta+\theta_0) = m\mathrm{C},$$

where m is the tangent of the angle which the θc line makes with the current axis, and θ is the temperature reckoned from 0° C. The values of m for the four series of experiments are in the approximate ratio :—

Meteoric ring (1st winding)	1
,, ,, (2nd winding)	1·25
Nickel-iron ring	1·35
Iron ring (see § 6, p. 39 below) . . .	1·60

whilst the corresponding values of θ_0 are 275°, 250°, 285°, and 270° respectively. From the latter numbers the curious result follows that the absolute temperature, between the limits specified, was directly proportional to the current producing it. In fact, it was seen from the data that the actual temperature between 300° C. and 800° C. produced by any current could be obtained correctly within a few degrees by determining a single temperature corresponding to a single given current, and then assuming in further experiments that the absolute temperature would be proportional to the current applied.

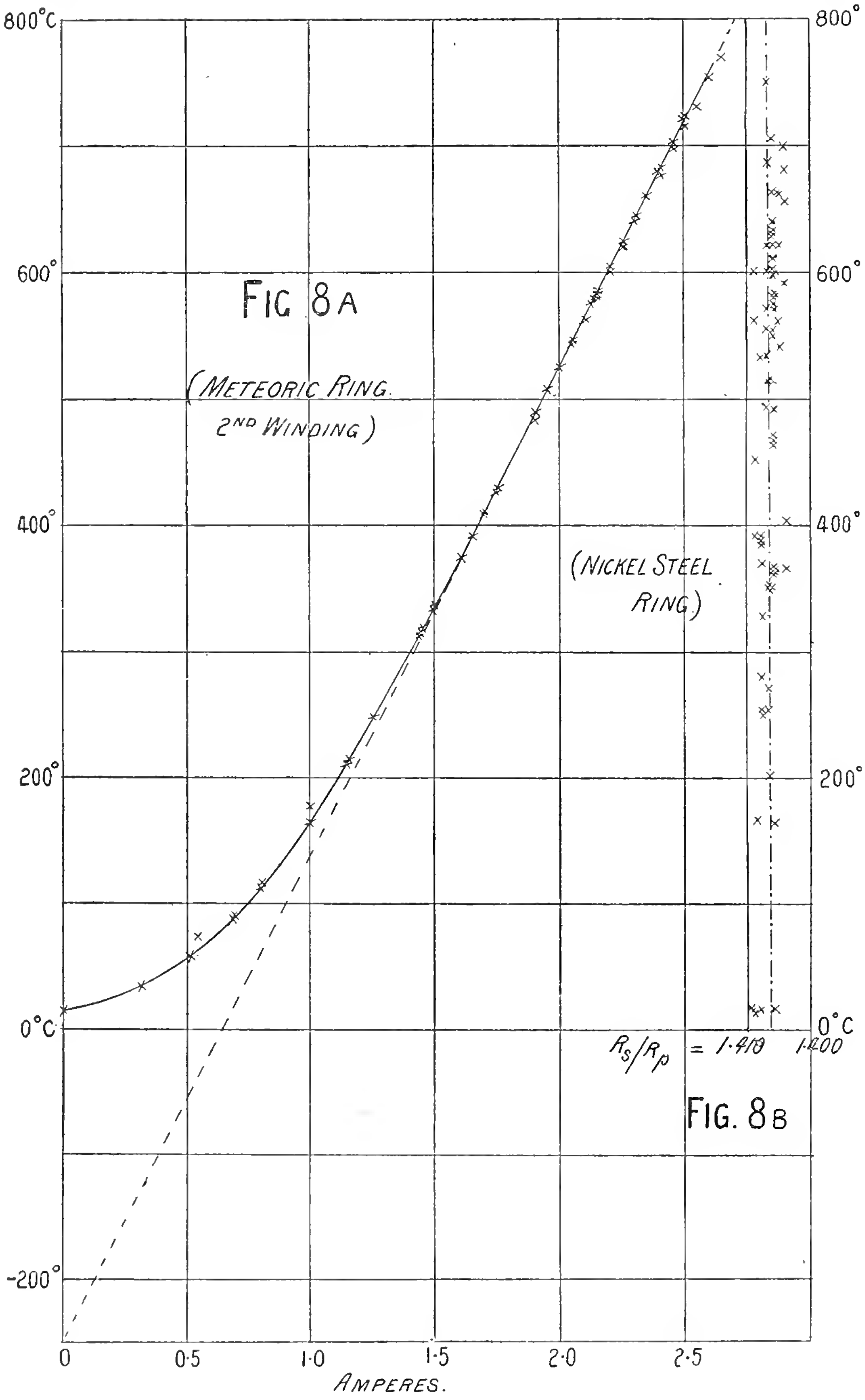
There were only a few measurements at temperatures above 800° C. The data seem to show that the θc curve slowly departs from linearity and becomes concave to the axis of temperature.

Below 300° C. the θc curve becomes convex to the axis of current. It would thus appear that the curve possesses an ill-defined point of inflexion somewhere between 300° C. and 800° C.

For temperatures below 100° C. the relation between θ and c is approximately parabolic.

§ 5. In practically all of the observations the resistance of the ring primary was measured in addition to that of the secondary. Corresponding values of the heating current were also tabulated. As it is impossible from want of space to give these data in the tables printed on pp. 42 to 47, the specimen curves shown in fig. 8 are reproduced to exhibit at a glance the degree of consistency attainable in the measurements. Fig. 8A, exhibiting the results of observations extending over three months, shows the extent to which the same heating current produced the same steady temperature on different occasions. Fig. 8B shows similarly the constancy of the ratio of the resistances of the primary and secondary at different steady temperatures, both coils being inside the heating coil and constructed of wire from the same reel.

§ 6. The dimensions of the rings used have already been given. In the first winding of the meteoric ring there were 34 turns of wire in the primary and 55 turns in the secondary, the diameters of the wires being 0·039 centim. and 0·033 centim.



respectively. In the second winding the numbers of turns were 31 and 51 respectively. In the case of the nickel steel ring the primary had 30 turns and the secondary 51, and each consisted of wire 0·032 centim. in diameter.

The constants (calculated by the method already described) by means of which corresponding values of μ and H can be obtained in absolute units from the observations are, in the case of the meteoric iron ring (first winding), given approximately by the equations

$$\mu = 135{\cdot}5 \times i_o d / i_p d_o,$$

$$\mathrm{H} = 28{\cdot}0 \times i_p,$$

in which d is the inductive effect (proportional to the sine of half the angle of throw) in the secondary circuit when the current i_p is established in the ring primary, and d_o is the corresponding inductive effect produced by a current i_o in the standardising solenoid. The corresponding constants in the other cases are:—Meteoric ring (second winding), 160·5 and 25·5; nickel steel ring, 166·4 and 24·8. (If the values of the constants were calculated in the ordinary way, the first would be about 0·6 per cent. higher and the second about 0·75 per cent. lower in each case.)

In the earlier experiments, of which the object was to examine how, for a constant value of H, μ varied with the temperature, the value of H chosen was 0·476, as being near the value of the Earth's field and corresponding with a convenient deflection—50 divisions—on the shunted voltmeter. In the experiments after the second winding of the meteoric ring the value of H used was unintentionally lower, viz., 0·433 instead of 0·476. This happened because the shunted voltmeter reading used was still 50 divisions, although the ring constant had become 25·5 instead of 28·0. In the experiments with the nickel steel ring, and also in some comparison experiments with a ring of nearly pure iron (of which further description is omitted for the present), the primary current was, in each case, adjusted so as to give a field as nearly as possible equal to that used with the meteoric ring after the second winding, and corresponded in each case to a field of 0·434 C.G.S. unit.

Owing to the difficulties of winding under the conditions necessary for work at high temperatures, the degree of accuracy of the constants calculated as above is not as great as is the accuracy, relative to one another, of the numbers proportional to μ. Consequently the actual values of the latter are not given, in most cases, in the tables showing the results of the measurements; but only the values of $i_o d / i_p d_o$, which are numbers proportional to them and which represent the direct results of the observations.

§ 7. In some cases, however, the actual values of the permeability, and not merely their relative values, are required approximately for the purposes of comparison. Thus the permeability of the meteoric iron was carefully determined at the conclusion of the experiments, after it had been subjected to repeated heatings, as described below, including a final annealing at 900° C. The permeability was also determined before the material received any thermal treatment beyond the slight warming that took place when the ring was cut out of the original block. The ring windings in these initial and final experiments were such that relatively accurate measurements could be made without difficulty. The resulting data show that, in round numbers, for H = 0·35 the permeability before heating was 120, while after heating it was 150; for H = 0·52 the corresponding numbers were 130 and 160. Hence there is no doubt that the permeability in weak fields was considerably higher after the thermal treatment than before.

The preliminary experiments (first winding) over a considerable range of temperatures show that the permeability at ordinary temperature can vary between considerable limits depending upon the thermal history of the specimen. Thus the greatest permeability observed was about 50 per cent. greater than the lowest. The approximate values of these extreme permeabilities were calculated to be 300 and 200 approximately (H = 0·48).

In the later experiments (second winding) the highest permeability observed at ordinary temperatures (H = 0·433) was about 278 (= 1·73 × 160·5), while the lowest was about 129 (= 0·8 × 160·5). Hence it is seen that the highest permeability at ordinary temperatures is more than double the lowest, and that the lowest corresponds approximately with the permeability of the meteorite in its original state.

From the same experiments it is seen further that the average value of the permeability at ordinary temperatures, after cooling from about 850° C., lies between the above values and is about 167 (= 1·04 × 160·5). This number is seen to be approximately correct from the results of the final measurements after annealing at 900° C., which gave μ = 154 for H = 0·36, and μ = 164 for H = 0·52.

The final measurements, after annealing at 900° C. in the case of the nickel steel, show also that the constant 166·4, calculated for the approximate conversion into absolute values of the data obtained during measurements over a wide temperature range, is not seriously in error. Thus the final measurements give μ = 179 for H = 0·37, and μ = 184 for H = 0·53, after annealing at 900° C.; while the earlier experiments fix the limits between which the permeability may lie after heating to about 800° C. as 174 (= 1·05 × 166·4) and 208 (= 1·25 × 166·4) for H = 0·43.

SECTION IV.—PERMEABILITY MEASUREMENTS BETWEEN 0° C. AND 850° C.

By S. W. J. SMITH *and* J. SATTERLY, *B.Sc.*

§ 1. In performing the experiments, of which the results are tabulated below, it was borne in mind that the permeability at a given temperature might not be free from a time effect. Hence, since in all probability the time rate of change of permeability at a given temperature would diminish fairly rapidly, and might become relatively small at the end of a comparatively short time, the ring was kept as long as was possible without prolonging the experiments unduly at a given temperature before the measurements were taken. Experience showed that consistent results were obtained if the material was allowed about two hours in which to acquire the temperature at which the measurements were to be made—the heating current being gradually increased to the necessary value. After the temperature, as shown by the resistance measurements, had remained practically constant for about half an hour, the throw due to induction in the standardising current was observed. The throws due to induction in the ring were measured after this, because they would be affected more by want of steadiness in the state of the ring. Finally the throw due to the standardising solenoid was checked and the temperature of the ring again noted.

In some of the later experiments, in which the time at disposal was more limited and it was necessary to get observations at a comparatively large number of points in succession, it was found that, if precautions were taken to reduce the rate of loss of heat by the ring, consistent results could be obtained, at moderately high temperatures, within an hour after the closing of the heating current circuit. In such cases the question whether there was a time effect was relatively unimportant.

§ 2. The majority of the temperature permeability measurements were performed under the influence of a constant field. In the earlier measurements the variation of μ with H was observed for values of H between 0·4 and 0·8 C.G.S. units; but the results of these observations, which are omitted from considerations of space, seemed to show that the information to be derived from them was not likely to be much greater than that derived from measurements under a constant field. The experiments were performed in the intervals between other work, and it would have been impossible to determine BH curves satisfactorily, over a wide range of values of H, in the time at disposal. It was therefore decided to aim only at fixing as accurately as possible, in the time available, the relation between the permeabilities at different temperatures, keeping the intensity of the field unchanged. The demagnetisation of the ring, observation of the inductive effect, and measurement of the resistance of the ring secondary were repeated in every case (sometimes as often as ten times) till there seemed no room for doubt that truly corresponding values of induction and temperature had been obtained.

§ 3. The data obtained from the experiments with the different materials are collected in the tables which follow.

METEORIC IRON (1st Winding).

First Experiments.

Number of experiment.	Temperature.	$\frac{\mu}{135\cdot5}$ (H = 0·475) C.G.S.
	° C.	
a	16·5	1·615
b	158	1·54
c	272	1·515
d	464	2·29
e	678	4·37
f	717	1·52
g	752	0·26
h	816	—
i	589	0·13 (H = 0·71)
k	15	1·56
l	621	4·58
m	669	4·71
n	551	2·96 (H = 0·54)

At the point numbered *h*, temperature 816°, the induction throw had become imperceptibly small. The current was lowered gradually, causing gradual fall of temperature, and observations were made continuously to find when perceptible ferromagnetism reappeared. There was a perceptible throw, when the resistance showed a temperature of 591°, corresponding to a permeability, on the above scale, of 0·05. At 589° the permeability was approximately 0·13 for a field strength of 0·71 C.G.S. units.

The experiment *n* was not strictly comparable with the others, as the apparatus had been partially dismantled in the month intervening between this experiment and that numbered *m*.

METEORIC Iron (1st Winding).

Later Experiments.

Number of experiment.	Temperature.	$\frac{\mu}{135\cdot5}$ (H = 0·475) C.G.S.	Number of experiment.	Temperature.	$\frac{\mu}{135\cdot5}$ (H = 0·475) C.G.S.
	° C.			° C.	
1	12	2·065	10	173	1·73
2	174	1·805	11	388	1·695
3	315	2·025	12	102	1·715
4	463	2·01	13	247	1·655
5	574	3·60	14	286	1·675
6	12·5	1·91	15	336	1·68
7	310	1·985	16	305	1·655
8	461	2·055	20	14	1·80
9	572	3·50	21	309	1·715

METEORIC Iron (1st Winding) (continued).

Later Experiments.

Number of experiment.	Temperature.	$\frac{\mu}{135\cdot5}$ (H = 0·475) C.G.S.	Number of experiment.	Temperature.	$\frac{\mu}{135\cdot5}$ (H = 0·475) C.G.S.
	° C.			° C.	
22*	638	4·4	45	578	0·58
23	576	0·58	46	640	0·88
24	528	1·805	47	575	0·63
25*	664	4·85			
26	552	1·79	48*	18	1·495
27	503	1·67	49*	20	1·555
28	480	1·63			
29	17	1·595	50	465	1·405
30*	314	1·725	51	576	2·81
31	545	1·855	52	466	1·72
32	528	1·88			
33	17	1·625	53*	18·5	1·995
34	168	1·545	54	20	1·665
35	20	1·625	55	5	1·54
36	284	1·57			
37	576	3·52	56	20	1·54
38	23	2·31	57	−10	1·545
39	—	2·175	58	—	—
40	163	1·925	59	18·5	1·57
41	307	2·05	60	—	—
42	386	2·04	61	18	1·55
43	434	1·85	62	—	1·545
44*	464	2·125	63	—	1·55

* After each of the experiments marked by an asterisk the ring was raised to a temperature of about 830° C., at which its permeability became too small to be measurable.

METEORIC Iron (2nd Winding).

First Experiments.

Number of experiment.	Temperature.	$\frac{\mu}{160\cdot5}$ (H = 0·433) C.G.S.	Number of experiment.	Temperature.	$\frac{\mu}{160\cdot5}$ (H = 0·433) C.G.S.
	° C.			° C.	
1	17	1·405	11	18	1·095
2	137	1·335	12	21	1·08
3	433	1·465	13	821	—
4	11	1·49	14	587	0·72
5	18	1·67	15	537	0·93
6	588	2·69	16	475	0·96
7	—	1·63	17	19	0·97
8	734	3·37 ?	18	923	—
9	—	1·26			
10	798	—			

The ring was heated to 522° C. between (4) and (5); but the permeability was not observed.

After (17) the apparatus was re-arranged and the ring was supported in the beaker inside an asbestos box slightly larger than itself. The rate of escape of heat at a given temperature was much reduced by the addition of this box, as is seen by comparison of (10) and (18), in which the same heating current was used. In the earlier experiments the only covering of the ring, inside the beaker, was a layer of asbestos paper.

METEORIC Iron (2nd Winding).

Later Experiments.

Number of experiment.	Temperature.	$\frac{\mu}{160\cdot5}$ (H = 0·433) C.G.S.	Number of experiment.	Temperature.	$\frac{\mu}{160\cdot5}$ (H = 0·433) C.G.S.
	° C.			° C.	
19	19·5	1·305	60	410	1·40
20	722	2·36	61	582	2·97
21*	769	0·087	62	676	3·49
22	575	0·68	63	11	1·085
23*	13	1·04	64	428	1·61
24	590	0·40	65	600	2·99
25	583	0·615	66	658	3·41
26	604	0·92	67	12	1·18
27	697	1·53	68	754	0·90
28	603	1·075	69	681·5	1·12
29*	—	0·98	70	619	0·99
30	588	0·68	71	526	0·72
31	700	1·38	72*	14·5	0·80
32	602	0·94	73	625	0·06
33	696	1·38	74	546	0·96
34	602	0·95	75	643	1·935
35	13	0·93	76	545	1·25
36	584	0·73	77*	13·5	0·945
37	644	1·13	78	545	1·085
38	710	1·505	79	649	2·10
39	13·5	0·96	80	552	1·36
40	584	0·52	81*	15	1·04
41	676	1·31	82	493	0·995
42	730	1·57	83	584	1·79
43	577	0·68	84	489	1·195
44	12·5	0·91	85	579	1·835
45	693	2·86	86	489	1·215
46	729	1·845	87	18	1·125
47	769	0·54	88	12	1·135
48	13	0·83	89	112	1·13
49	681	2·76	90	216	1·18
50	715	1·96	91	334	1·36
51	639	1·85	92	449	1·495
52	524	1·12	93	621	2·98
53	337	0·87			
54	about 105	0·80	94	12·5	1·47
55*	12	0·83	95	625	2·91
56	561	0·78	96	450	1·45
57	524	0·98	97	333	1·41
58	434	0·95	98	212·5	1·265
59	12·5	0·98	99	118	1·23

* After each of these experiments the temperature of the ring was raised to about 850° C.

METEORIC Iron (2nd Winding) (continued).

Later Experiments.

Number of experiment.	Temperature.	$\frac{\mu}{160\cdot5}$ (H = 0·433) C.G.S.	Number of experiment.	Temperature.	$\frac{\mu}{160\cdot5}$ (H = 0·433) C.G.S.
	°C.			°C.	
100	12	1·465	149	15·5	1·560
101	700	3·58	150	165	1·555
102	661	2·71	151	389	1·555
103	507	1·37	152	249	1·505
104	9·5	1·11	153	15	1·525
105	667	3·16	154	722	3·065
106	605	2·715	155	601	1·915
107	480	1·39	156	715	2·645
108	394	1·21	157	17	0·96
109	178	1·185	158	719	2·81
110*	14·5	1·21	159	602	1·885
111	16	1·035	160	718	2·52
112	131	1·03	161	20	0·88
113	315	1·195	162	720	2·71
114	429	1·28	163	679	2·36
115	16·5	1·255	164	622	2·065
116	429	1·27	165	678	2·58
117	544	2·25	166	730	2·165
118	623	2·83	167	16	0·83
119	16	1·725	168	719	2·495
120	33·5	1·725	169	680	2·40
121	57·5	1·715	170	624	1·97
122	89·5	1·685	171	15·5	0·82
123	16·7	1·71	172	722	2·675
124	114	1·72	173	661	2·315
125	166	1·73	174	602	1·87
126	212	1·79	175	659	2·41
127	15·7	1·69	176	15	0·835
128	261	1·865	177	723	2·735
129	317	1·925	178	623	2·01
130	390	1·835	179	526	1·225
131	425	1·49	180	622	2·10
132	482	1·645	181*	14·7	0·845
133	17	1·66	182	587	0·965
134	391	1·56	183	604	1·20
135	319	1·50	184	624	1·42
136	17·5	1·60	185	680	2·11
137	430	1·485	186	622	1·62
138	375	1·315	187	564	1·24
139	250	1·465	188	16·7	0·845
140	19·5	1·575	189	430	1·39
141	624	2·815	190	683	3·10
142	427	1·345	191	432	1·085
143	390	1·320	192	681	3·06
			193	434	1·055
144	15	1·565	194	683	3·07
145	89·5	1·55	195	18	0·95
146	334	1·80	196	625	2·76
147	408	1·575	197	73·5	1·165
148	334	1·475	198	16	1·245

* After each of these experiments the temperature of the ring was raised to about 850° C.

NICKEL Steel.

Number of experiment.	Temperature.	$\frac{\mu}{166 \cdot 4}$ (H = 0·434) C.G.S.	Number of experiment.	Temperature.	$\frac{\mu}{166 \cdot 4}$ (H = 0·434) C.G.S.
	°C.			°C.	
1	3·5	1·195	49	14	1·145
2	15·5	1·215	50	749	0·395
3	163	1·385	51	655	0·76
4	402	1·365	52	571	1·705
5	538	2·465	53	466	1·49
6	15	1·41	54	367	1·38
7	548	2·58	55	272	1·245
8	698	1·81	56	106	1·06
9	770	—	57	14	0·97
10	639	0·44	58	366	1·37
11	533	1·89	59	598	4·03
12	280	1·39	60	388	1·875
13	12·5	1·125	61	595	4·09
14	493	1·935	62	389	1·96
15	641	4·90	63	14	1·11
16	13	1·235	64	603	4·26
17	251	1·65	65	516	2·925
18	386	2·275	66	349	1·875
19	13·5	1·265	67	12	1·11
20	789	0·05	68	603	4·39
20*a*	799	0·015	69	613	4·62
20*b*	811	—	70	13	1·10
21	671	0·043	71	624	4·99
22	573	2·40	72	642	5·46
23	514	2·395	73	12·5	1·045
24	387	1·85	74	671	5·72
25	253	1·615	75	689	4·53
26	15·5	1·255	76	558	2·90
27	252	1·575	77	454	1·80
28	367	1·80	78	312	1·39
29	470	1·97	79	14	0·85
30	532	2·84	80	—	0·845
31	594	4·45	81	13	0·845
32	14·5	1·415	82	328	1·39
33	489	2·685	83*	663	5·24
34	608	4·99	84	554	2·55
35	13·5	1·43	85	14·5	0·945
36	706	2·61 2·42	86	558	2·985
37	639	2·77	87	662	5·95 5·84
38	554	2·185	88*	14·5	0·925
39	468	1·60	89	602	2·65
40	368	1·49	90	683	4·60 4·52
41	202	1·165			
42	13	0·95	91	597	3·09
43	365	1·355	92	664	4·34
44	574	3·65	93*	10	0·765
45	14	1·095	94	624	1·88 1·91
46	166	1·315			
47	384	1·92	95	686	3·005
48	570	3·74	96	620	2·33

* After each of these experiments the temperature of the ring was raised to about 850° C., at which the permeability was imperceptible.

NICKEL Steel (continued).

Number of experiment.	Temperature.	$\frac{\mu}{166\cdot 4}$ (H = 0·434) C.G.S.	Number of experiment.	Temperature.	$\frac{\mu}{166\cdot 4}$ (H = 0·434) C.G.S.
	°C.			°C.	
97	14	0·795	103	12	1·04
98	581	3·46	104	581	3·83
99	12·5	0·945	105	12·5	1·05
100	580	3·74	106	580	3·82
101	12·5	1·02	107	13	1·05
102	580	3·81			

In experiments 36, 87, and 90, the permeability seemed to fall, with lapse of time, from the higher to the lower value; but the temperature coefficient of μ is very large between 650° C. and 750° C.

In experiment 94 the permeability seemed to be rising gradually at 624° C.

§ 4. The series of curves, given below, figs. 9 to 22, show the results of the attempt to represent graphically, by continuous curves, the thermomagnetic properties of each material. The number of the experiment to which each point corresponds is shown in each of the curves drawn; but, because of the use made of the curves later and also because there are some relationships which cannot be represented graphically, it is necessary to state the connection between the tables and the curves at greater length than would otherwise be required.

§ 5. *Meteoric Iron* (1*st Winding*).—See fig. 9.

The sequence of all the experiments tabulated will be clearer if an account is given of the reasons why they were performed in the order shown.

The permeability at ordinary temperatures was determined, under my supervision, by Mr. W. H. N. JAMES, with the results already given (see Section II., § 2, p. 27). The experiments over a wider temperature range, after the coils had been rewound by Mr. JAMES and myself, had only extended to a few isolated measurements when it became impossible for him to take further part in the work. With a view to completing the experiments, I again set up the apparatus when time permitted and took the observations lettered *a*, *b*,...*n*, of which the record is given in the first table. The observations *a*, *b* and *c* showed the variation of μ at the lower temperatures. The region in which the permeability began to rise rapidly was marked by *d* and *e*; *f*, *g* and *h* marked the temperature range over which the permeability dropped from near its maximum value until it practically disappeared. The observations at *i* showed that the temperature lag in the reappearance of permeability, common to artificial nickel-iron alloys containing less than 25 per cent. of nickel, was shared by the

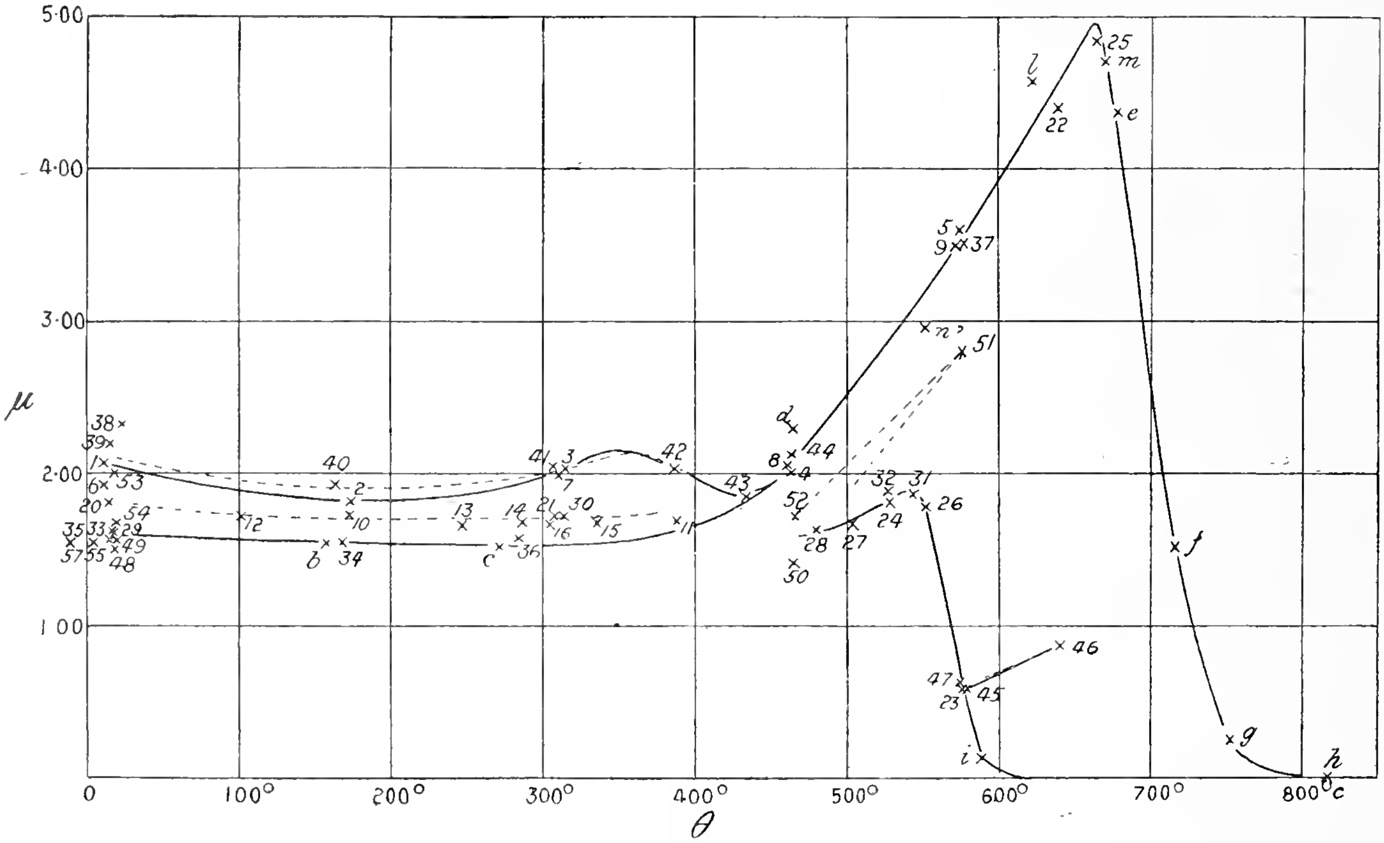


Fig. 9. Meteoric iron (1st winding).

Relation between permeability (H = 0·48 C.G.S. approximate) and thermal treatment. C.G.S. values of μ = ordinates × 135·5 (approximate).

meteorite. The observation k showed that the permeability, after slow cooling from a temperature beyond the critical point, was nearly the same as that first observed. The observations l and m were next made in order to get values of μ near the temperature of maximum permeability.

After the experiments just described, no further measurements were taken until the isolated observation represented by n was made with the object of filling a gap, at about 550° C., in the previous observations. After being allowed to cool from the temperature just stated, the ring was left for about three months without further observation. The experiments represented by the numbers 1 to 63 were then begun. I was surprised to find that the permeability at ordinary temperature was about 30 per cent. higher than the value (k) last observed at that temperature, and it seemed as if the permeability had risen in that proportion in the three months during which the ring had been left undisturbed. It seemed advisable to examine whether this apparent time effect, so pronounced at ordinary temperature, was accompanied by any change in the variation of μ at higher temperatures. The experiments 2, 3, and 4, 5 showed an apparently anomalous position, with respect to one another, of the points 3 and 4. For this reason the observations at these temperatures were repeated (see 7 and 8), as was that at the higher temperature (see 9). It was found that although the permeability at ordinary temperature seemed to change appreciably, the permeabilities at 315° C., 460° C. and 575° C. (approximately) were subject to little variation under the treatment undergone.

The observations 10 to 16 were undertaken to find, if possible, how the permeability varied between 100° C. and 400° C. There seemed to be no sudden or irreversible changes; but the permeability was now intermediate between its earlier values and those observed after the lapse of 3 months. No experiments were made between those numbered 16 and 20, except to explore without success for a possible increase of permeability in the neighbourhood of 300° to 350° C.

The experiments 20 to 37 were undertaken with the object of finding again, under the apparently changed condition of the ring, the variation of permeability as the temperature was raised above the critical point, and, also, the manner in which the permeability reappeared as the ring was gradually cooled.

The observations 23, 24, and 26 to 28 seemed to show that there was an appreciable difference between the hysteresis in the reappearance of magnetism in the meteorite and that in nickel steel of similar composition examined by HOPKINSON. In HOPKINSON's curve for a 4·7 per cent. nickel steel (H = 0·12 C.G.S.) the portions of the $\mu\theta$ curve below 600° C. (for rising and falling temperatures respectively) would apparently be nearly superposable, whereas in the present case they were not. It was thought that the distance between the points 26, 24, &c., and corresponding points on the curve of rising temperatures might possibly have been less if the ring had been cooled more slowly. For this reason the observations were repeated (see 31 and 32), and the ring was kept for several hours at temperatures near 550° C., after cooling, in order to find whether a gradual rise in permeability could be detected. The value of μ at the end of two hours was, however, in each case not perceptibly different from its value after two hours more, and hence, if the change in question was actually occurring, it was of a much more gradual nature than those represented in the curves described here, and probably, also, in the curves described by HOPKINSON.

The observations 33 to 35, and also 29, showed that the state of the material (after gradual cooling from about 820° C.) was practically identical with its state at the beginning of the observations three months before. (A preliminary heating beyond the critical temperature had preceded the latter observations.)

The observation 37 showed that the permeability at 575° C. was practically the same as when heating took place from the state represented by Experiment 1, at which the permeability was much higher than at a, 29, 33, &c.

Thus it appeared that, although there was considerable uncertainty concerning the nature of the variation of μ with θ, especially at temperatures below 500° C., the material was not one in which the properties were continually changing in an arbitrary manner owing to gradual oxidation, to disintegration, or to some other effect increasing with time and arising possibly from an unassignable cause.

The permeability was next measured (38 and 39) after the temperature had again fallen (from 37) to that of the air. It was found now to be even greater than in Experiment 1. It thus became clear that the relatively great value of the latter was not due to a time effect lasting over three months (as was at first thought possible), but to the fact that the material had been allowed to cool uninterruptedly from a temperature of about 550° C. (see Experiment *n*). If the permeability had been measured immediately after this cooling it would apparently have been found to be as high as it was three months later.

An attempt was now made to find how the permeability of the ring in its new state altered with rising temperature. The result is shown in Experiments 40 to 44. These explained the apparently anomalous position of the points 3 and 4, which had been noticed at the time the latter were observed. The permeability varied slightly with rising temperature, falling at first and then rising. Between 300° and 400° C. it appeared to reach a maximum value, and then, beyond 400° C., it fell comparatively rapidly to a well-defined minimum value at about 435° C., beyond which the permeability quickly rose. It is obvious, therefore, from the data and the figure, that the points 3 and 4 lay on a $\mu\theta$ curve corresponding exactly with that just described. These experiments showed again that the behaviour of the material was definite, and, at the same time, that the permeability at a given temperature was strongly influenced by the previous thermal history of the material.

The effect of interrupted heating having been so pronounced, I next examined whether any noticeable effects resulted from interrupted cooling. After the ring had been heated beyond the point at which the ferro-magnetism disappeared it was allowed to cool gradually until a temperature was reached at which the ferro-magnetism had begun to increase rapidly with fall of temperature. The permeability was measured at this temperature, and the ring was then heated through about 60° C. and kept at a constant temperature for about two hours, after which the permeability was again measured. The ring was then allowed to cool, and the permeability was measured a second time at the temperature at which the cooling was interrupted. The permeability rose considerably on heating, but on cooling it fell again practically to the same value as it had when the cooling was interrupted (see 45, 46 and 47). This result agreed with the qualitative diagram given by GUILLAUME as representing the behaviour of irreversible nickel steels under similar treatment (*cf.* C. E. GUILLAUME, 'Congrès International, Paris, 1900').

On cooling to the air temperature, the permeability was found to be a little lower than the lowest value previously recorded (see 48). Subsequent reheating beyond 820° C. and uninterrupted cooling restored the permeability at ordinary temperature to the normal value. Hence interrupted cooling had slightly lowered the subsequent ordinary temperature permeability (*cf.* § 7 below, p. 54, also Section VI., § 11, p. 90).

The object of the next experiments was to observe the effect of cooling interrupted at a temperature below that at which the permeability ceased to rise with falling temperature and began to diminish. The temperature chosen was about 465° C., at which the permeability was unexpectedly low, possibly because of insufficient preliminary heating (see later). On raising the temperature to about 575° C., the permeability rose rapidly, and on allowing the temperature to fall to 465° C. again it was found that, although the permeability fell considerably, it was now 25 per cent. greater than the value at this temperature when the cooling was interrupted. Subsequently, when the temperature had fallen to that of the air the permeability was much larger than it would have been if the cooling had been uninterrupted (see 53). It was, however, less than the value that would have been obtained by a further reheating to 575° C., as previously described (*cf.* 37 and 38).

The ring was now heated again above the critical temperature, and allowed to cool uninterruptedly when, as shown in the table, it showed the old permeability, at the ordinary temperature, corresponding with such treatment. (The first value, 54, was probably too high because the ring had not been allowed sufficient time to acquire a steady state.) The ring was then cooled to −10° C. without showing any appreciable variation of permeability. The object of this cooling was to find whether there was any sign of the comparatively sudden increase of permeability observed by HOPKINSON in the case of a 25 per cent. nickel steel.

Finally the ring was left undisturbed for some weeks, and the permeability was found to be the same at the end as at the beginning of this period.

§ 6. The experiments just described showed that the permeability was subject to peculiar, but nevertheless definable, variation as the result of thermal treatment. Repetitions of a given process had led always to practically the same result, and hence, apart from the question of the interpretation of the data already obtained, it seemed worth while to study further, at various temperatures, those effects of interrupted heating and cooling which had been shown already, at some temperatures, to be accompanied by marked changes in the magnetic properties of the material. Thus, for example, it still remained to examine the effect of cooling from a temperature between that corresponding to the maximum permeability and that at which the permeability became imperceptible. I was anxious also to test more fully whether the remarkable reversibility between the two steep branches of the $\mu\theta$ curves, described by GUILLAUME in the case of artificial alloys, was shown by the meteorite. But at this point it became necessary, through want of time, to abandon the work or to enlist the services of another observer. Fortunately, Mr. J. SATTERLY, B.Sc., formerly a student and assistant at the Royal College of Science, volunteered to complete the examination of the meteoric iron on the lines proposed and also, if necessary, to test in a similar way a sample of artificial nickel iron, of nearly the same composition (see Section I., § 7, p. 26), which I had obtained for this purpose.

After Mr. SATTERLY had made a few preliminary observations corroborating those described above, the insulation of the ring secondary for some reason became defective, and it was decided to take off all the coils and re-wind them. The original wires were used for the primary and secondary coils, but a coil with a greater number of turns was substituted for the original heating coil.

Except for occasional assistance, nearly all the permeability observations after the second winding were made by Mr. Satterly.

§ 7. *Meteoric Iron* (*2nd Winding*).—See fig. 10, &c.

An attempt has been made, in the series of figures numbered 10 to 16, to represent the relations between the data obtained after the second winding. It required more consideration than might appear necessary at first sight to decide upon the form of some of the curves, and they may not be altogether free from such errors of interpretation as are difficult to avoid in the attempt to construct continuous curves from a set of discontinuous observations.

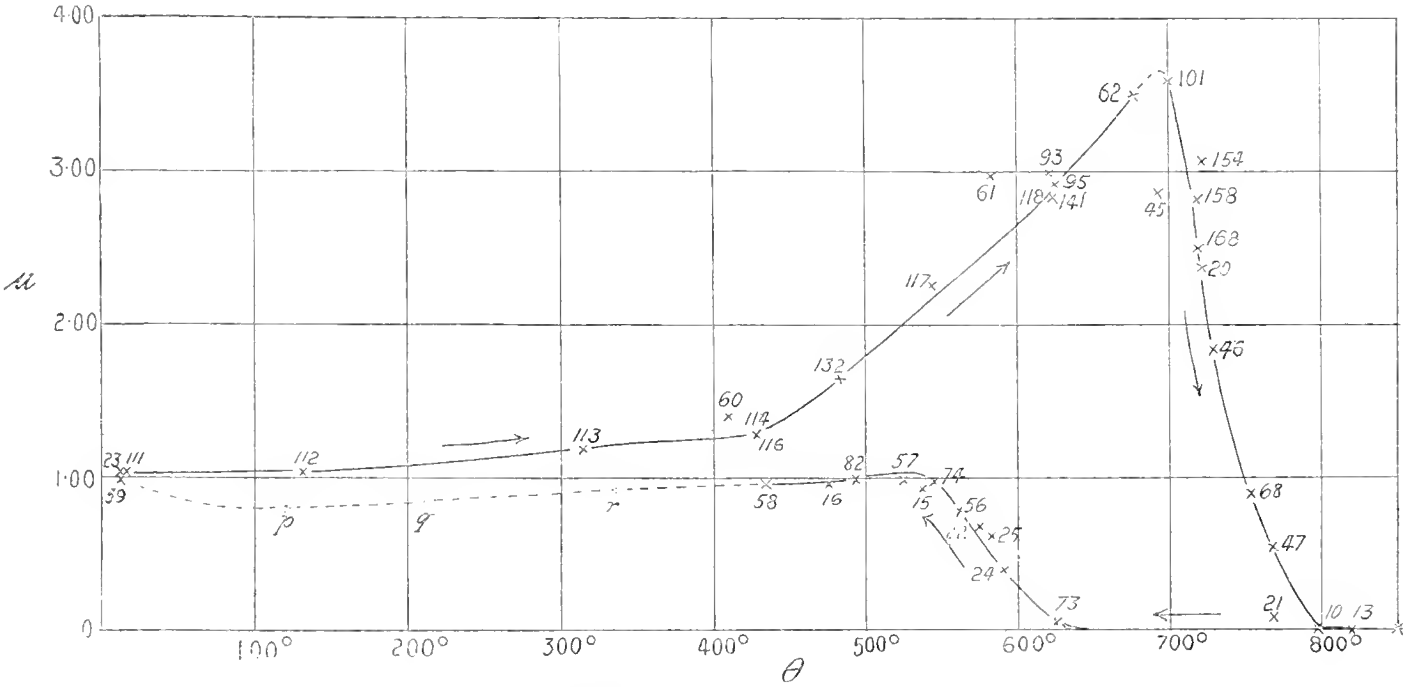


Fig. 10. Meteoric iron (2nd winding).

Field intensity $= 0\cdot 43$, C.G.S. values of $\mu =$ ordinates $\times$ $160\cdot 5$ (approximate).

Variation of permeability with temperature during continuous cooling from about 850° C., and continuous reheating to same temperature.

Fig. 10 is intended to represent the variation with change of temperature of the permeability of the meteorite as it is cooled continuously from above the critical temperature to the temperature of the air, and then heated uninterruptedly until its ferromagnetism again becomes too small to be measurable. The numbers of the experiments upon which the curve is based are given in the figure. It will be seen that the greatest amount of uncertainty as to the form of the curve is in the part representing the cooling from 400° C. to 15° C. The similarity between 28 and 29 (1st winding), and between 58 and 59 (2nd winding) seemed to suggest that the permeability would not vary appreciably over this range. From subsequent data and from reasons given later it seems possible, however, that the permeability *may* become perceptibly less at intermediate temperatures than it was found to be at 400° C. and 15° C.

On a later occasion, after thermal treatment, to be described, the permeability variation was observed during cooling at a number of temperatures intermediate between those just stated. The initial and final permeabilities (see 96 and 100, fig. 13) in this case bear practically the same relation to one another as the permeabilities (at 58 and 59) represented in fig. 10. *The positions of the points p, q and r were calculated on the assumption* that the ratio of the permeabilities, at corresponding temperatures in the two cases, remained the same throughout the cooling as at 450° C. and 15° C. The lack of experimental data that might be of interest was not noticed until after the apparatus had been dismantled.

The general form of the $\mu\theta$ curve having been again approximately determined, the first experiments after re-winding were made to test, from points in the region where the permeability is rising rapidly during cooling, for the reversibility described by GUILLAUME (see above, § 6, p. 50). The experiments were not completely satisfactory on account of the difficulty of keeping the temperature absolutely constant for a considerable time. In the measurements given under the first winding the second value of the permeability at the original temperature of interrupted cooling was slightly greater than the first, but as both observations lay in a region where the permeability varied rapidly with temperature, it was difficult to decide whether the variation was not strictly reversible. In order to make the test less difficult

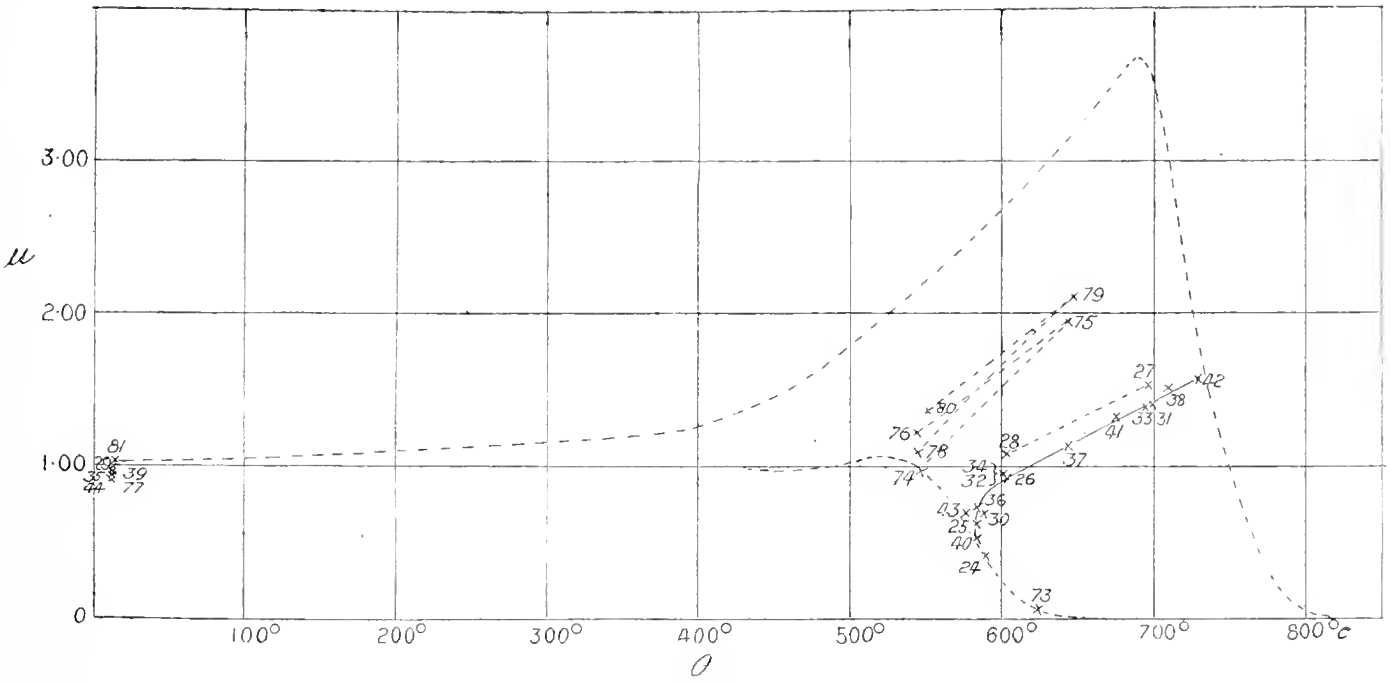


Fig. 11. Meteoric iron (2nd winding).

Cooling from 850° C. interrupted at 580° C. and at 550° C. (respectively).

Effect of subsequent reheating and cooling.

experimentally the observations were made at about 600° C. and 700° C., *i.e.*, at temperatures where the permeability was not subject to rapid variation. The experiments 26, 27 and 28 seem to show that there is distinct irreversibility on the first cooling from 700° C., but the experiments 31 to 34 seem to show that, after the first reheating and cooling, the subsequent variations are practically reversible—the permeability being subject at most to a very slight rise.

An attempt was made to determine how the curve of alternate heating and cooling just described departs from and returns to the steeper curve of continuous cooling. It was here that the uncertainty arising from the difficulty of maintaining a constant temperature became most pronounced, but from the experiments 40 to 42, in conjunction with those just quoted, it would seem that at the beginning of the first reheating the permeability rises more rapidly than it does subsequently (fig. 11), and that the changes in permeability variation are certainly less abrupt than in the qualitative diagrams given by GUILLAUME. (Experimental magnetic data are not given in any of the papers by GUILLAUME to which I have had access. It is worth notice that permeability measurements may reveal changes of internal structure too small to be detectable by other methods. *Cf.* Section VII., § 12, p. 101 below). The data of fig. 11 are not sufficient to show how the curve of falling permeability, passing through 42 and 43, meets the curve of continuous cooling, but it is noteworthy, as in the first winding, that interrupted cooling and subsequent treatment as above is followed, in every case, by a lower permeability at ordinary temperatures than if the cooling had been continuous from beyond the critical point (see later, Section VI., § 11, p. 91).

It was next intended to test for reversibility, on cooling and reheating, from a point in the region (between 700° C. and 800° C.) in which the permeability falls rapidly with rising temperature. For this purpose the points 45 to 47 (see also fig. 10) were taken in order to get the general position of the region in question. The heating was not continued beyond about 770° C. (47) owing to want of time. It was noticed that, as the result of uninterrupted cooling from 770° C., the permeability at ordinary temperature was lower than any value previously obtained, and 20 per cent. lower than that obtained after uninterrupted cooling from temperatures above that at which ferromagnetism becomes imperceptible.

The ring was then reheated to a point on the falling branch of the curve (about 720° C.) and then allowed to cool without intermediate reheating. Measurements of permeability were taken from time to time until the air temperature was reached. The results are shown in Experiments 50 to 55. The permeability at ordinary temperature was again exceptionally low and practically identical with that obtained just previously after uninterrupted cooling from 770° C.

The permeability at ordinary temperature was now raised, by treatment similar to that described under the first winding (see 67), and the ring was then heated to about 755° C. and again cooled uninterruptedly (except for stoppages at three temperatures for the measurement of permeability) to the temperature of the air. The resulting permeability was again very low (see 72) and practically equal to that obtained after cooling from 770° C. and 720° C. respectively (see fig. 12).

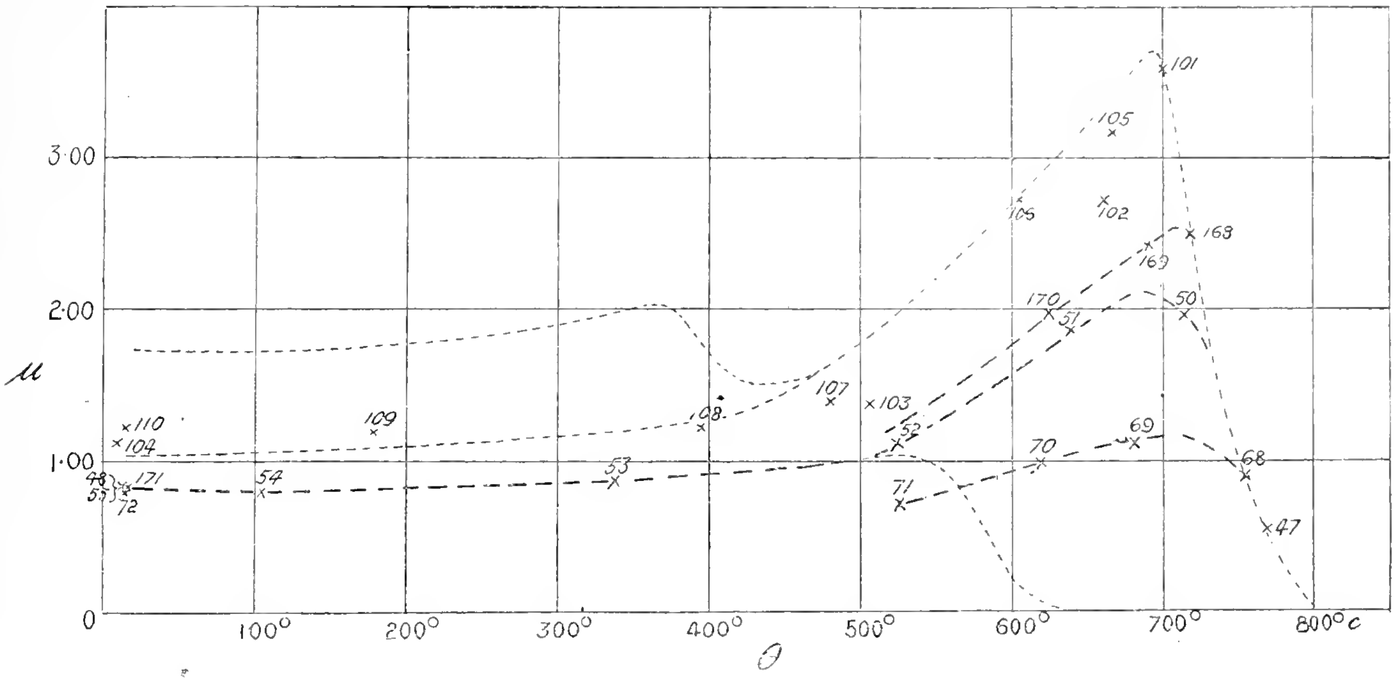


Fig. 12. Meteoric iron (2nd winding).

Reheating to 850° C. interrupted at temperatures between 700° C. and 800° C.

Variation of μ during subsequent continuous cooling to air temperature.

On fig. 12 there are plotted also the results of a much later set of observations (168 to 171) which lead to the same result as the above sets. They serve further to show the constancy in the behaviour of the material.

Apart from showing that very low and nearly equal values result from uninterrupted cooling from a temperature between 700° C. and 800° C., the numbers just given show that GUILLAUME's qualitative diagram does not represent exactly what happens in the present case; since, if it did, the permeability at ordinary temperature in each of the above cases should be the same as that obtained after uninterrupted cooling from above 850° C.

The experiments 74 to 80 (shown in fig. 11) prove that, when cooling from 850° C. is interrupted near the temperature at which the permeability ceases to rise, subsequent reheating is accompanied by irreversible change of permeability. The nature and extent of this irreversibility is shown further in fig. 13. From the experiments 82 to 86 it is seen that, after a second reheating, the state of the material is practically reversible and the hysteresis with respect to temperature has almost disappeared, being ten times smaller after the second reheating from 490° C. than after the first (*cf.* 31 to 34 and also experiments described later).

Fig. 13 shows also the result of the first attempt to trace exactly how heating interrupted in the neighbourhood of 600° C. results in an exceptionally high

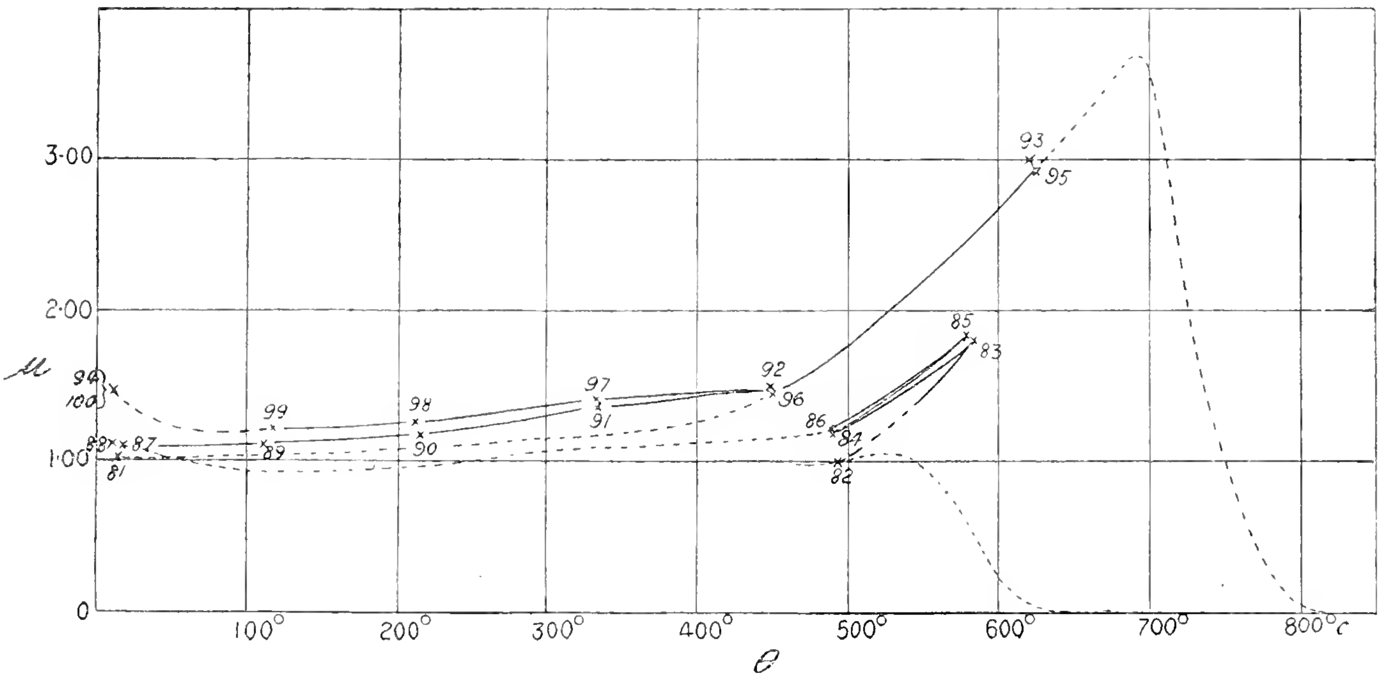


Fig. 13. Meteoric iron (2nd winding).

Variation of μ with θ below 500° C.—

(i) when cooling from 850° C. is interrupted at 500° C.

(ii) when reheating to 850° C. is interrupted at 625° C.

permeability at ordinary temperature (*cf.* 1st winding). From the data 88 to 100 it is seen that the greater part of the increase takes place during the time that the material is cooling from below 100° C. to the temperature of the air (*cf.* 99 to 100).

The experiments 101 to 110 (fig. 12) seem to show that uninterrupted cooling from

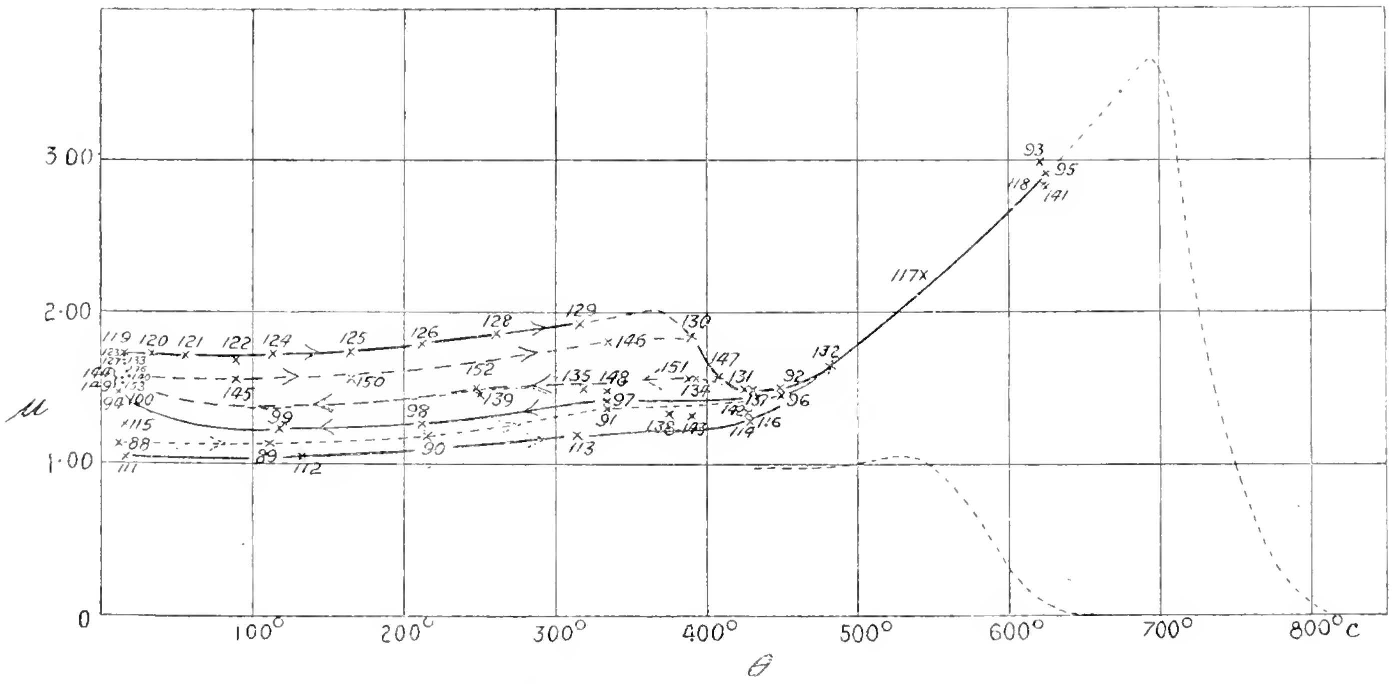


Fig. 14. Meteoric iron (2nd winding).

Curves showing the variation, at temperatures below 500° C., of the permeability obtained after cooling from about 600° C.

a point on the rapidly descending part of the $\mu\theta$ curve is accompanied by a lowering of permeability at ordinary temperature which a single reheating to 670° C. is not sufficient to remove (see, however, Section VI., § 8, p. 88 below).

The experiments 111 to 119 (fig. 14) show the full effect of heating interrupted at about 620° C. on the ordinary temperature permeability—the point 111 having been obtained after uninterrupted cooling from beyond the critical point, and the point 115 after heating interrupted at about 430° C.

The experiments 119 to 129 (fig. 14) show how the permeability now changes with rising temperature, 123 and 127 showing that the change is reversible, and 121, 122 and 124 that there is apparently a minimum permeability in the neighbourhood of 100° C. The experiments 130 to 132 corroborate the sudden fall and subsequent rise, with a minimum permeability at about 440° C., noticed after similar treatment in the case of the first winding (*cf.* fig. 9).

Observation 133 shows that on cooling from 480° C. (132), after the permeability has begun to rise again, the air temperature permeability is practically the same as at the outset. The observations 134 to 136 were made to examine the effect of cooling from a point near 400° C., at which temperature the permeability of the ring in its new condition was falling rapidly with rising temperature. These show that there is a well-marked temperature lag, the returning permeability at 300° C. being much below the permeability at the same temperature during heating, although the permeability eventually rises, at the air temperature, nearly to its original value. Experiments 137 to 140 show a similar effect, with a further slight decline in the ordinary temperature permeability. A subsequent heating to 625° C. (141) did not have much effect upon the air temperature permeability (144). The experiments 144 to 153 corroborate those already made.

The result of the experiments plotted in fig. 14 is, therefore, to show that reheating to 625° C. is followed by a large increase in the permeability at ordinary temperature. The greater part of this increase takes place, irreversibly, below 100° C. The permeability remains high upon subsequent reheating until a temperature of about 400° C. is reached; but beyond 500° C. the permeability is the same as it was before the treatment which resulted in the relatively high permeabilities at lower temperatures. Further, the additional permeability produced as above is subject to approximately reversible variations, over temperatures between those of its appearance and disappearance, of the same kind as those observed at higher temperatures (*cf.* figs. 11 and 15).

An attempt was made next to determine whether the variation of permeability, as the temperature fell from between 700° C. and 800° C., was reversible in the meteorite, as it is stated to be by GUILLAUME in artificial alloys. The results of the experiments are difficult to represent in a single diagram (fig. 15); but the correct conclusion seems to be that in each case there is not strict reversibility and that the permeability is greater on reheating than it was at the corresponding temperature during cooling

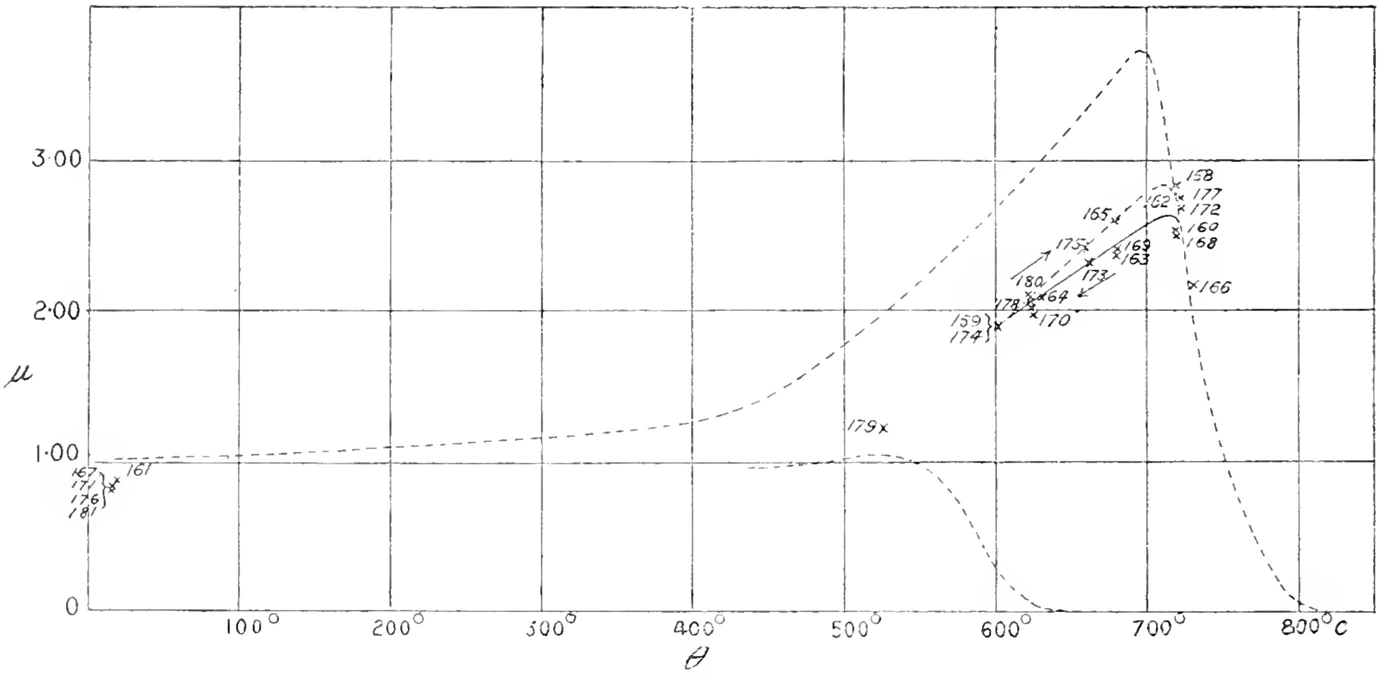


Fig. 15. Meteoric iron (2nd winding).
Reheating to 850° C. interrupted between 700° C. and 800° C.
Effect of subsequent cooling and reheating.

(*cf.* 163 to 165, 173 to 175, and 178 to 180). It is noticeable, corroborating this view, that the readings at the air temperature (167 and 171) after continuous cooling are practically identical with previous values (*cf.* 48, 55, 72) obtained under similar treatment, while the values at 176 and 181 (after interrupted cooling) are each slightly larger, showing that the effect of reheating to a temperature in the

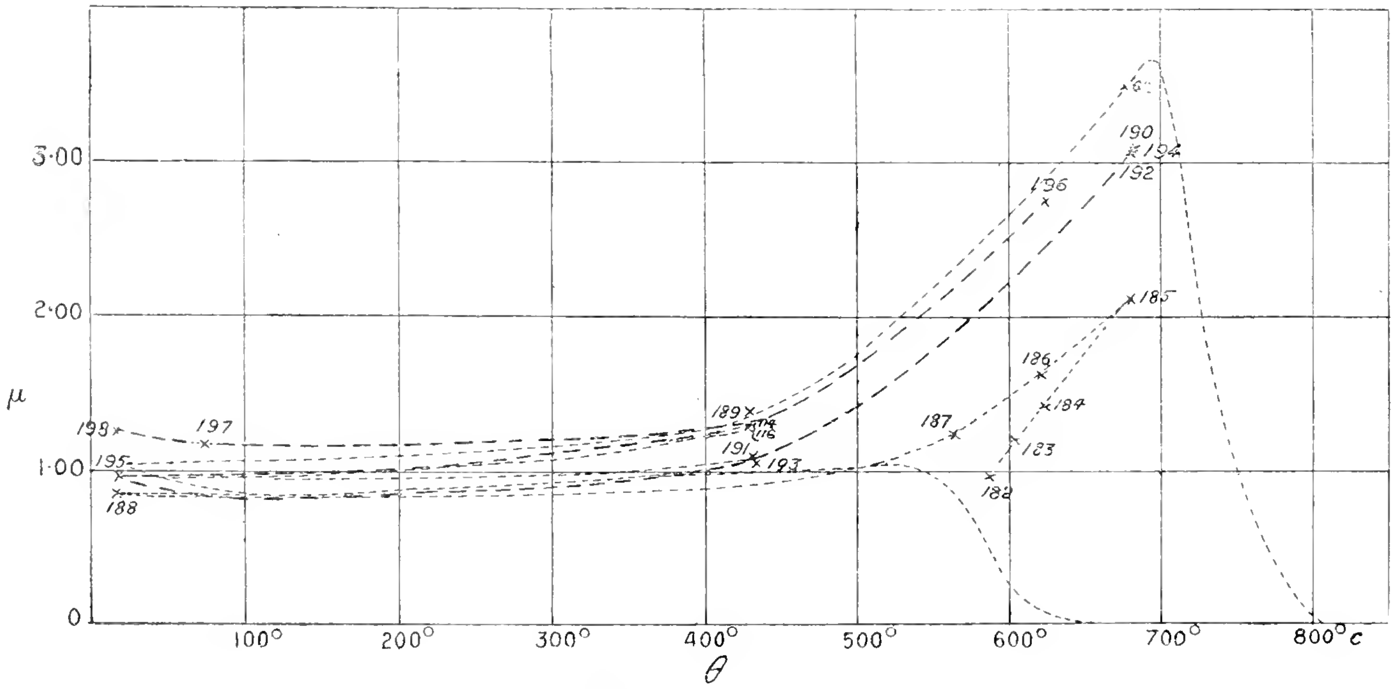


Fig. 16. Meteoric iron (2nd winding).
Effect upon permeability of temperature change alternating between (i) 430° C. and 680° C., (ii) 15° C. and 625° C.

neighbourhood of 650° C. has the effect of slightly raising the air temperature permeability obtained on subsequent continuous cooling. Hence, under the conditions described, it may be said that the change in question is not strictly reversible, although by analogy, from results already given, it is probable that a few reheatings and coolings would result in subsequent practical reversibility.

The final experiments, 182 to 198, show the effect of alterations over various ranges of temperature. The points 182 to 187 (fig. 16) show the irreversibility already noted (*cf.* 78 to 80). Points 190 to 194 show, over a wider range than 85 and 86, that the permeability becomes reversible under repetition of heating and cooling between about 430° C. and 680° C. It is not until the temperature is lowered beyond 430° C. that the permeability shows any further rise on heating. The observations 195 to 198 show, over a wider range, the same irreversible effect as occurs between 182 and 187.

§ 8. *Hadfield* 5·8 *per cent. Nickel Steel.*—(See fig. 17, &c.)

The object of the experiments on the nickel steel was to enable a comparison to be made, under conditions as far as possible identical, of the thermomagnetic properties of natural and artificial nickel-iron alloys of similar percentage composition. The rings were almost identical in size, were heated in the same way, and had primary and secondary coils as nearly as possible alike.

The nickel steel contained almost the same percentage of iron as the meteorite, but about 1 per cent. less of nickel. It contained about 0·7 per cent. of manganese and smaller quantities of carbon and silicon. All these substances were absent in the meteorite, which contained, however, about 0·4 per cent. of cobalt.

The experiments 1 to 8, in the table of results, were made with the ring in the unannealed condition in which it was after construction, and serve only to show that the permeability begins to rise rapidly at about 500° C., and that the maximum had been passed at 700° C. It seems worth while to note (although the data upon which the inference is based are few in number) that the positions of the points 1 to 7 (see fig. 17) suggest a closer resemblance, below 550° C., between the properties of the nickel steel in its unannealed state and those of the meteoric iron than was found after the annealing of the former. The possible significance of this will be seen later (*cf.* Section VI., § 12, p. 92, and Section VII., § 14, p. 102).

The experiments 9 to 13 were made to find the effect of annealing, and those from 14 to 16 to show the effect of reheating interrupted at a temperature in the region in which the permeability is increasing rapidly with rise in temperature. The results are shown in fig. 17, in which the outer dotted curve, running from 15° C. to 810° C., is drawn in order that the relation between the present data and those obtained later may be represented in the figure.

The ring was next annealed at a higher temperature (see 20*b*), as it was doubtful whether, in Experiment 9, the ring had been heated to a temperature at which

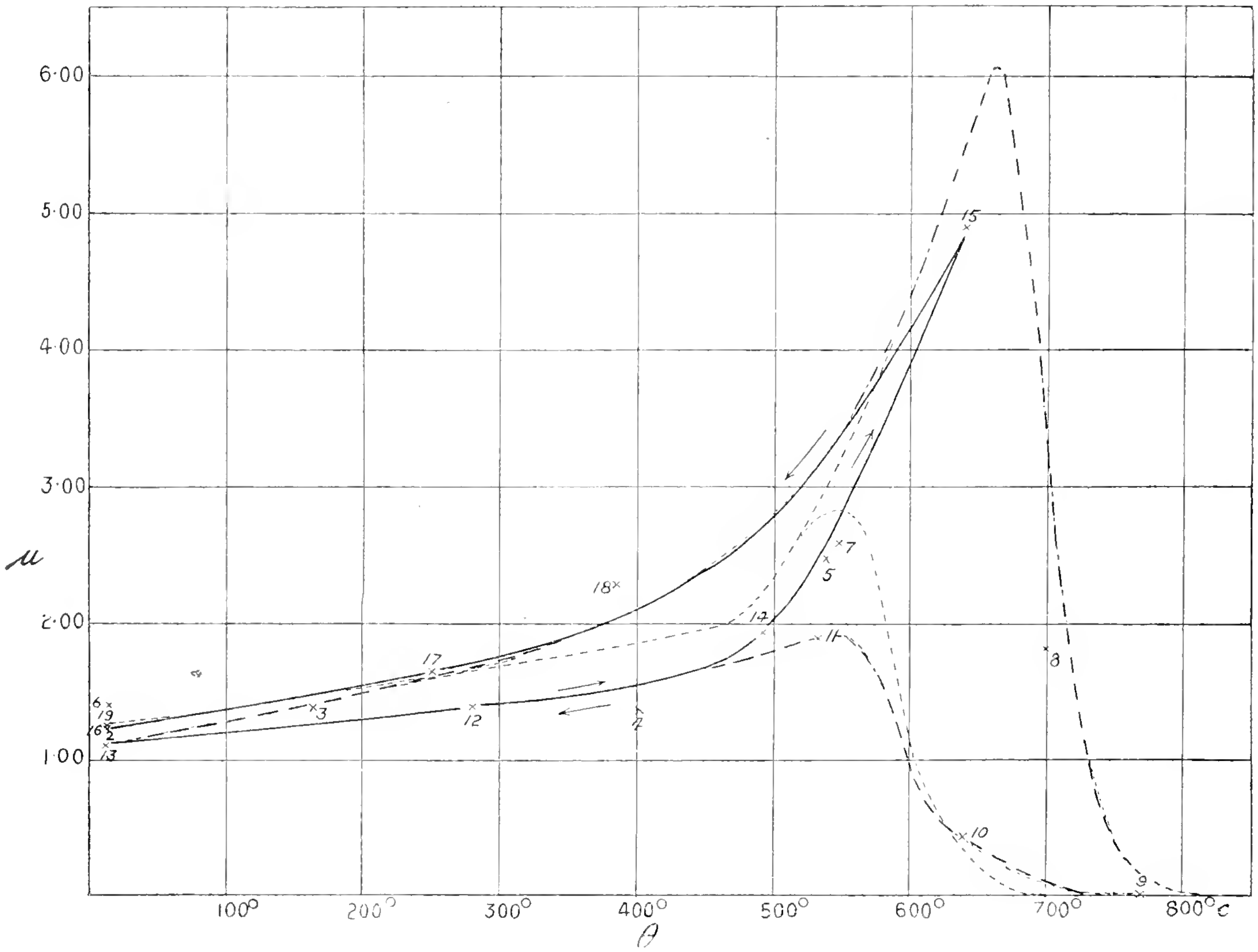


Fig. 17. Nickel steel.

Field intensity = 0·43, C.G.S. values of μ = ordinates × 166·4 (approximate).

Effect of cooling from 770° C. and of subsequent reheating to 640° C.

ferromagnetism had completely disappeared. The temperature of reappearance and the subsequent variation of permeability during cooling were again observed (see fig. 18, 21 to 26) and the variation of permeability during subsequent reheating to 600° C. is shown by the observations 27 to 31.

It is seen from the observations 21 to 31 that the rising and falling permeability curves are practically superposable (below about 550° C.) as in the curves given by Hopkinson, which, as already described, differ from those for the meteoric iron.

The permeability at air temperature resulting from heating interrupted at 600° C. is shown in 32, and the value upon subsequent heating to 490° C. is shown in 33. The air temperature permeability is seen to be raised comparatively little by treatment identical with that which produced a large increase in the case of the meteorite; but the permeability at 490° C. (33) is notably larger than the values obtained previously at about the same temperature (*cf.* 23 and 29). A second cooling from about 600° C. produced a slight further rise in the air temperature permeability (*cf.* 32 and 35). The other data shown in fig. 18 will be referred to later (see Section VI., § 10, p. 90).

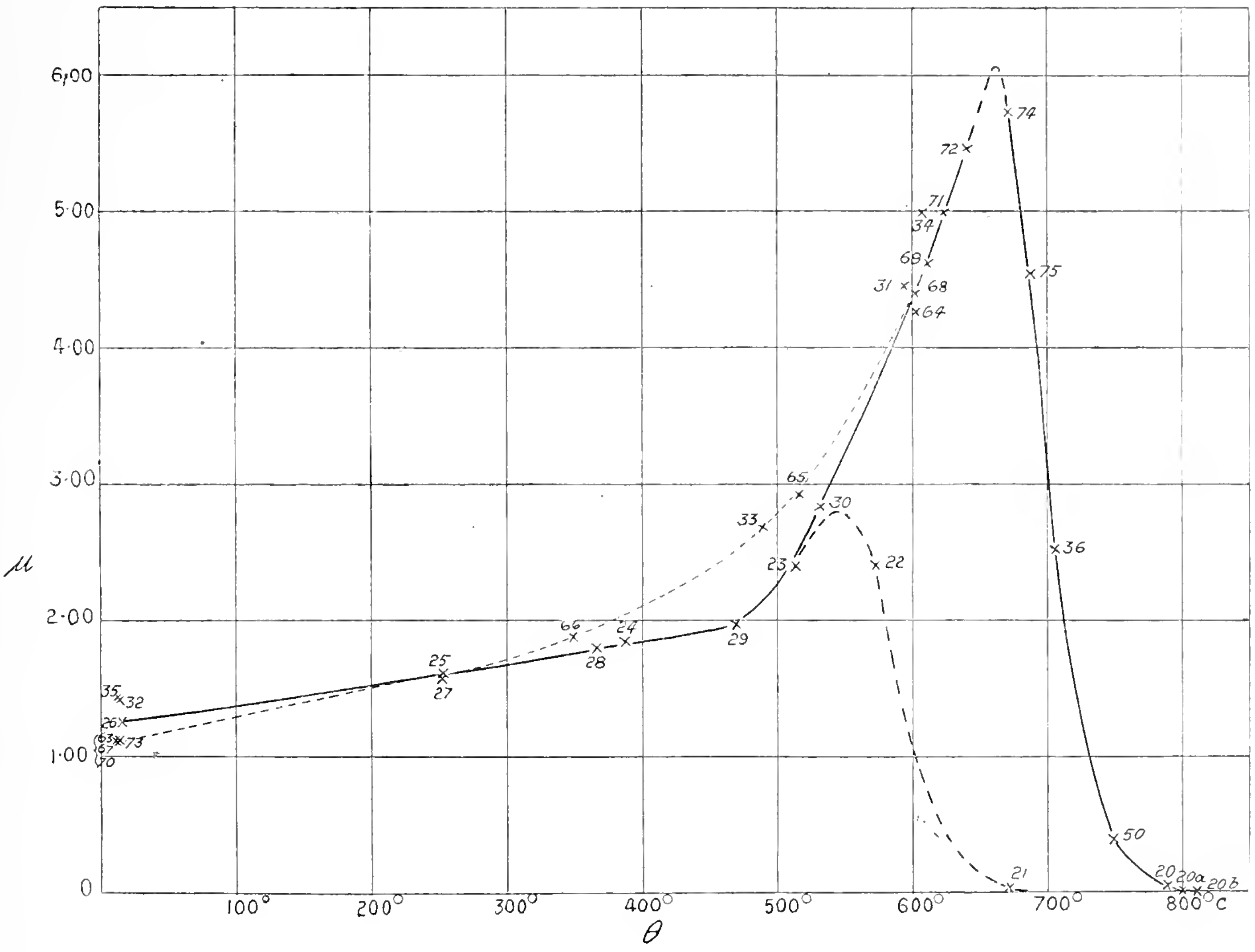


Fig. 18. Nickel steel.

Curve showing relation between permeability and temperature during continuous cooling from about 810° C. and continuous reheating to same temperature.

The next experiments were made to find what happened on cooling from a temperature (705° C.) in the region (about 680° C. to 800° C.) in which the permeability is falling rapidly with increase in temperature. The results are shown in fig. 19 (observations 36 to 42). It is seen that the air temperature permeability is reduced by this treatment, as in the case of the meteorite (*cf.* 26 and 42). The ring was next reheated to 570° C., when it is seen that the permeability rose rapidly beyond 450° C. as before (*cf.* fig. 18), and then allowed to cool to the air temperature. This procedure raised the air temperature permeability about 15 per cent. A subsequent reheating caused a further rise of 5 per cent. (*cf.* 45 to 49). Hence the effect of alternation of temperature between given limits is of the same character as in the case of the meteorite.

Fig. 20 shows the effect upon the subsequent permeability of heating interrupted at a higher temperature than in fig. 19, but at which the permeability was still measurable, viz., 750° C.

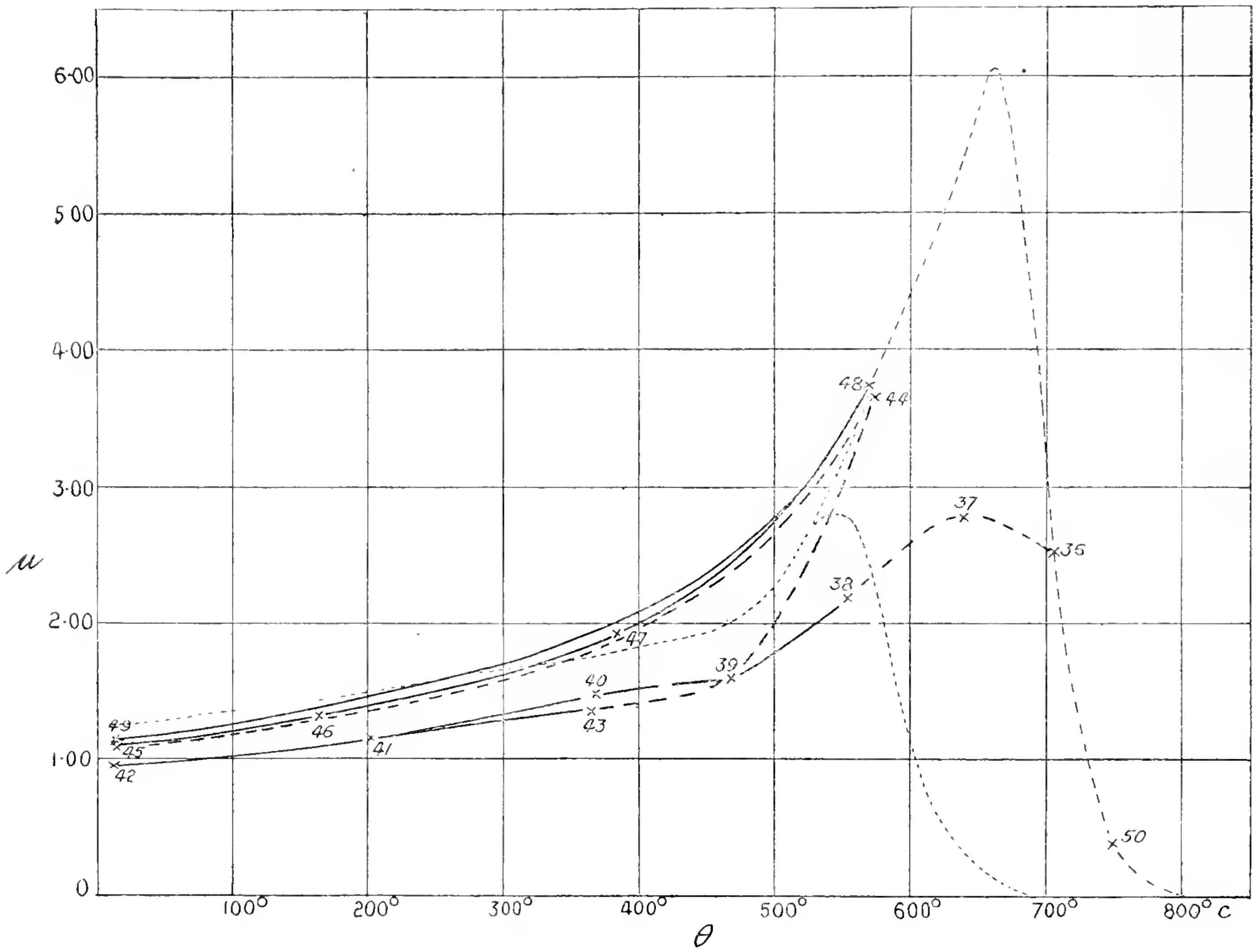


Fig. 19. Nickel steel.

Reheating to 810° C. interrupted at 705° C.

Variation of μ during subsequent continuous cooling to the temperature of the air.

Effect of two subsequent reheatings to 570° C.

The air temperature permeability was again very low and, although slightly greater than that previously obtained (42), was about 28 per cent. lower than the value obtained after cooling from beyond the temperature at which the ferromagnetism becomes imperceptible. The ring was now reheated to about 600° C., as in the previous case, when the permeability seemed to vary reversibly below 400° C. (*cf.* 54 and 58), as it did under similar circumstances in the previous experiments, and to rise rapidly between 400° C. and 600° C. [It will be seen (Section VI., § 10, p. 90) that the points 53 to 58 lie nearly in a straight line, as do the points 24 to 29, fig. 18, and 41 to 43, fig. 19, and that these lines meet approximately at the same point on the axis of temperature produced.] The ring was next subjected to alternate heating and cooling between 400° C. and 600° C. (*cf.* 59 to 62) with the result, as shown in fig. 20, that the permeability rose at first rapidly and then, during subsequent alternation, very slowly (*cf.* 58, 60, and 62).

The ring was then allowed to cool to the air temperature, when its permeability

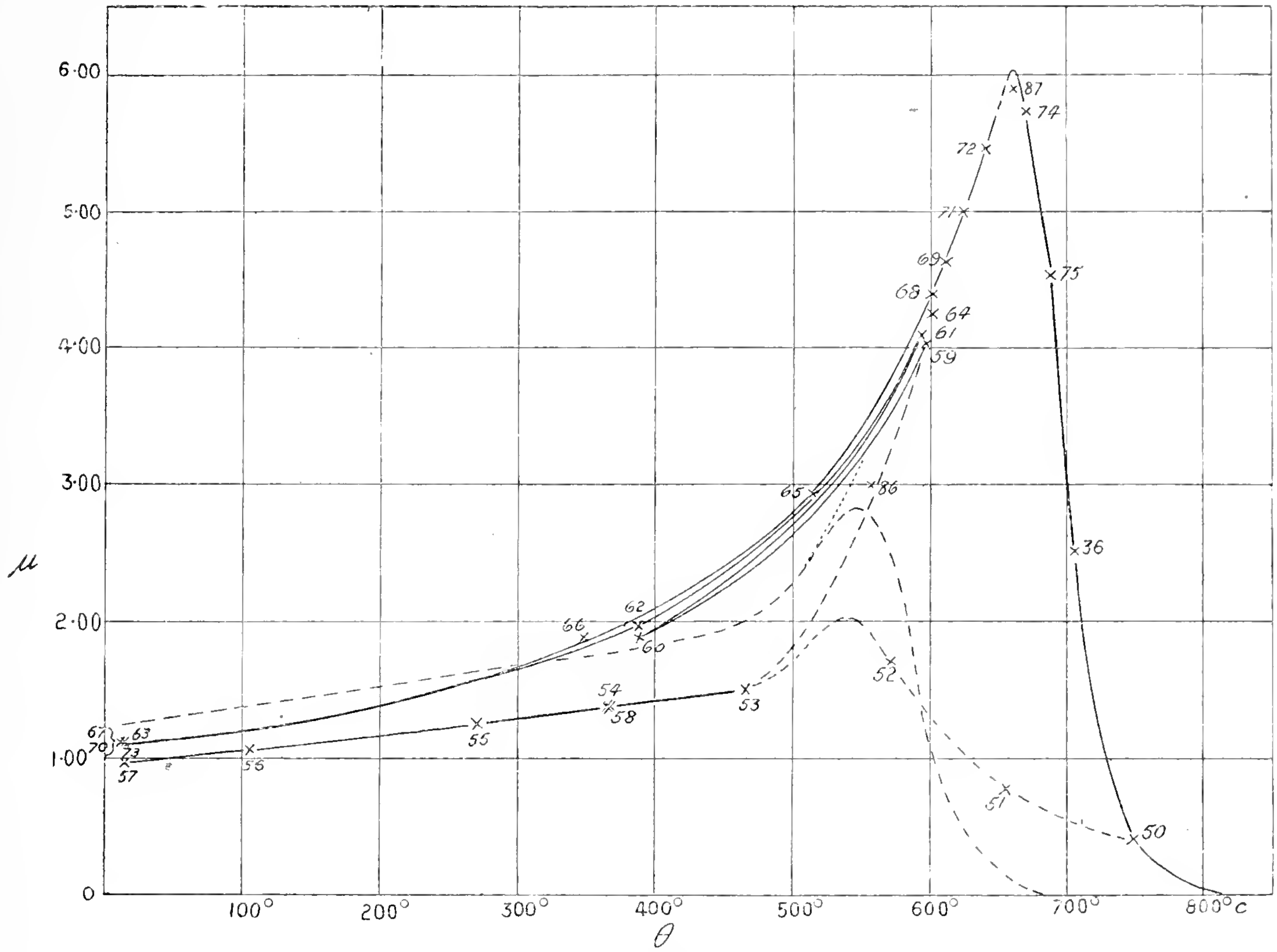


Fig. 20. Nickel steel.

Reheating to 810° C. interrupted at 750° C.

Variation of μ during subsequent cooling.

Effect of reheating to 600° C. and of subsequent alternation of temperature between 400° C. and 600° C.

Effect of subsequent alternation between 15° C. and 650° C.

was found to be practically the same as it was under corresponding circumstances previously (*cf.* 45 and 63).

The ring was next subjected to alternation of temperature between 15° C. and 600° C. and finally between 15° C. and about 650° C., the permeability being measured at various intermediate temperatures as shown. It is seen that, as a result, the permeability acquires a practically steady state at all temperatures below that of maximum permeability. This state is represented by the curve passing through the points 63 to 73, fig. 20, and shown by dotted lines in the other figures. (It is noticeable that, if the ring is heated nearly to its temperature of maximum permeability, the subsequent air temperature permeability is slightly less than when the temperature is not raised beyond 600° C.—compare 63, 67, and 70 with 73. A possible interpretation of this will be found later, see Section VI., § 8, p. 88.)

The ring was now heated to a temperature (690° C.) not far beyond the maximum

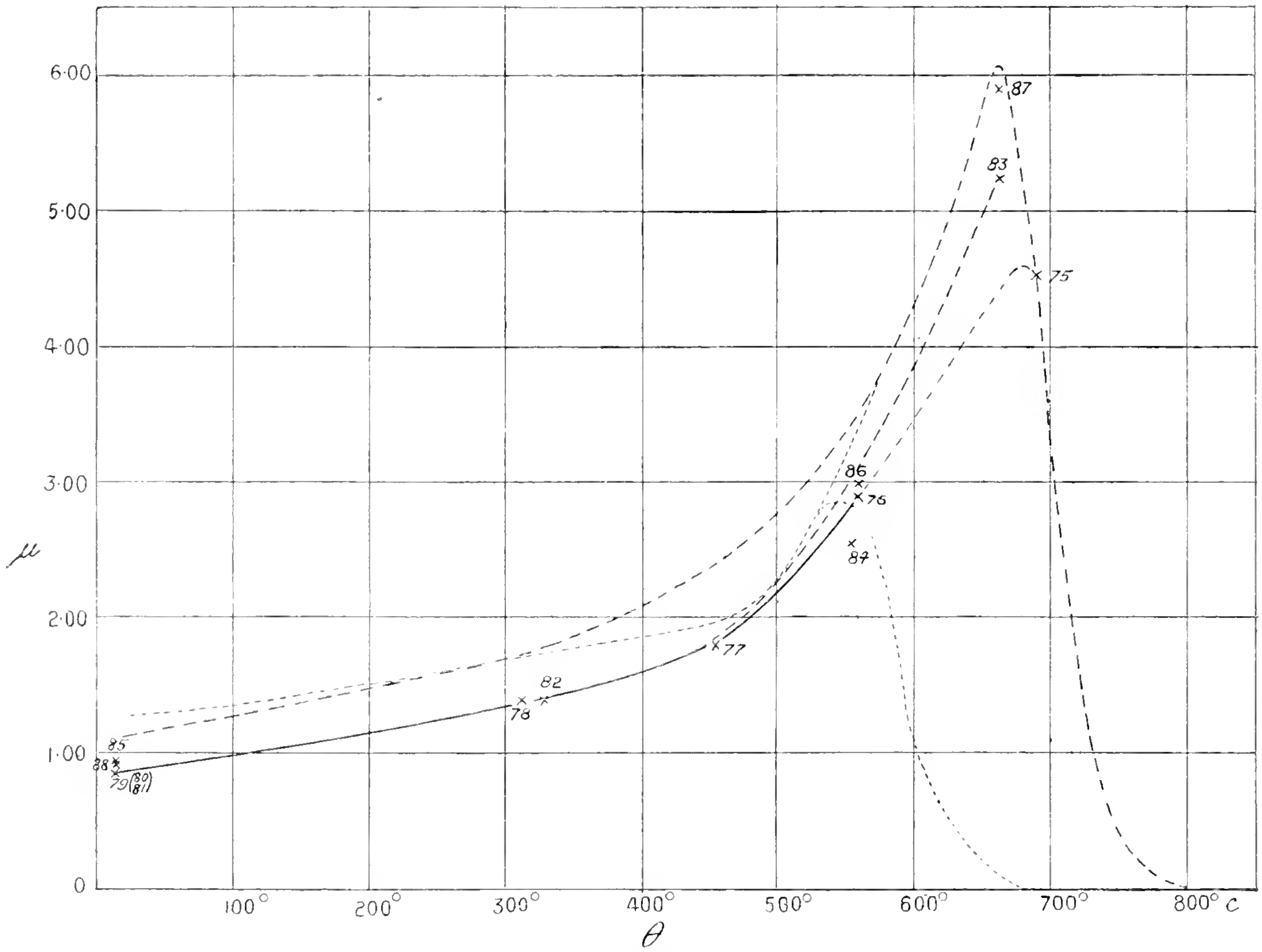


Fig. 21. Nickel steel.

Reheating to 810° C. interrupted at 690° C.

Variation of μ during subsequent cooling to 15° C. and reheating to 660° C.

and then allowed to cool, with stoppages for the measurement of permeability. The results are shown in the points 76 to 79 (fig. 21). The air temperature permeability was now even lower than after previous coolings from 705° C. and 750° C. respectively (*cf.* 79, 42, and 57). The ring was then heated beyond the critical point and then allowed to cool to the temperature of the air. The permeability was raised about 10 per cent. by this process, but was still comparatively low. Reheating to 660° C. did not seem to raise the permeability (*cf.* 85 and 88), but the effect of heating to a lower temperature, *e.g.*, 600° C., was not observed. The latter treatment, as can be inferred with certainty from the earlier and later experiments, would have raised the permeability at the air temperature.

The sets of observations 75 to 79, 36 to 42, 50 to 57, 9 to 13, and 20 to 26 show that the air temperature permeability after cooling from beyond the temperature of maximum permeability is greater in proportion as the temperature from which the cooling begins approaches that at which ferromagnetism has disappeared.

From the above results it can be inferred that the permeability does not vary

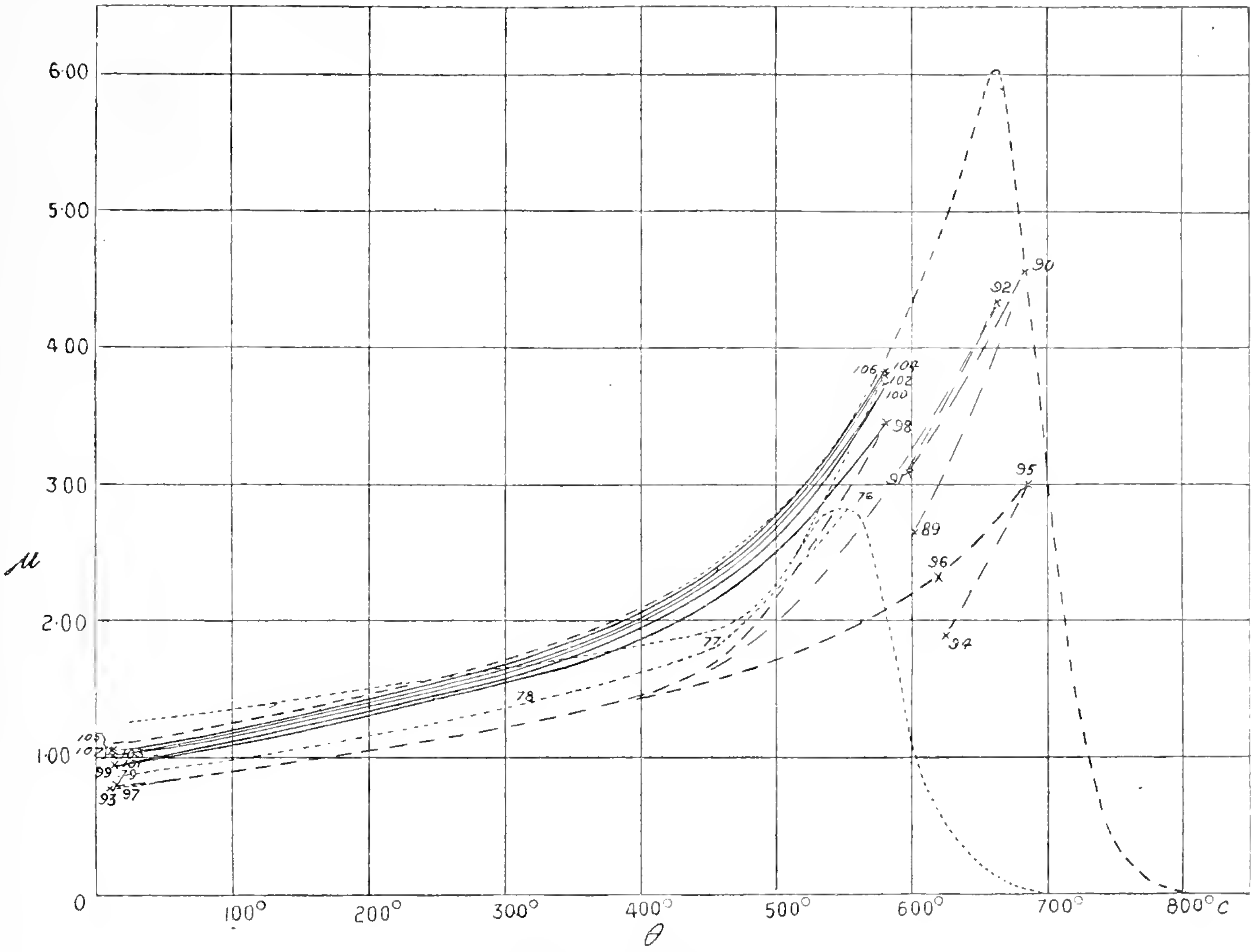


Fig. 22. Nickel steel.

Effect of interrupted cooling and of subsequent alternation of temperature between 15° C. and 580° C.

reversibly (in the time occupied by the experiments) over temperatures between those of the rising and falling permeability curves of fig. 18. This inference is seen to be correct from the results of the observations 89 to 92 and 94 to 96. It is noticeable (fig. 22) that, as in the case of the meteorite, but to a greater extent, alternation of temperature between the falling and rising permeability curves is followed by a relatively low permeability at the air temperature (see 93 and 97). (*Cf.* Section VI., § 11.) The effect of a single reheating to 580° C. upon the air temperature permeability is shown in the experiments 97 to 99, and the effect of subsequent alternation of temperature between 13° C. and 580° C. is shown in the observations 99 to 107. As in all previous cases, the permeability change produced by alternation diminishes rapidly from one alternation to the next, and, in the present case, after three alternations further change was imperceptible. The observations are also consistent with the inference from previous experiments that the irreversible increase of permeability does not begin until, on the first reheating, some temperature between 400° C. and 500° C. is attained.

The permeabilities finally obtained at 580° C. and 13° C., after five alternations between these limits (see 106 and 107), lie only slightly below the curve, already determined, which represents the condition of the material when its permeability varies reversibly between the air temperature and a temperature not far below that of maximum permeability. (There is evidence of a slight diminution of permeability, during the course of the experiments, possibly due to oxidation or to some other cumulative effect.)

SECTION V.—THE RELATIONS BETWEEN THE PROPERTIES OF NICKEL-IRON ALLOYS CONTAINING DIFFERENT PERCENTAGES OF NICKEL.

§ 1. A study of the relations between the temperatures of appearance and disappearance of magnetism in nickel-iron alloys containing different percentages of nickel (*cf.*, *e.g.*, OSMOND, 'Revue Générale des Sciences,' vol. XIV., p. 865, 1903) shows that as the percentage of nickel increases up to some value not far from 27, the temperatures of appearance and disappearance become continuously lower and more widely separated from each other.

When the percentage of nickel exceeds 30 the temperature of appearance is only slightly below the temperature of disappearance of magnetism, and OSMOND is of opinion, in agreement with GUILLAUME, that the temperatures would practically coincide if the rate of change of temperature were made sufficiently slow to avoid possible difference between the temperature of the thermocouple and that of the bar of the alloy under examination. According to this view the alloys can be divided into two classes, namely, those containing not more than 27 per cent. of nickel, which are *irreversible*, and those containing more than 27 per cent., which are *reversible*.

§ 2. These results suggest that the percentage at which transition occurs from one class of alloys to the other corresponds with a eutectic point. Following ROOZEBOOM, OSMOND represents the "equilibrium curves" for the nickel-iron alloys diagrammatically, as in the figure below (*cf.*, however, § 19, p. 77).

The curve ABCD is obtained from the magnetic measurements above described. The dotted curves AE, FCD are theoretical in the first instance, and their positions are not assumed to be more than qualitatively correct. Their properties may be indicated briefly by supposing a line drawn through any temperature θ, parallel to the axis of temperature, and cutting the different curves of the figure in p, q, r, s, t, and u respectively. At this temperature θ solid solutions containing θq, θr, and θu per cent. of nickel are, respectively, in equilibrium with "mixed crystals" of iron and nickel containing θp, θs, θt per cent. of the latter.

The curves are drawn in accordance with the theorem, confirmed by experiment on mixed substances which deposit mixed crystals, that when the transition temperature of a substance (*e.g.*, Fe) is reduced by the addition of a second substance (*e.g.*, Ni) with which it forms mixed crystals, the crystals in equilibrium with the solution must contain a less percentage of the second substance than the solid solution—the

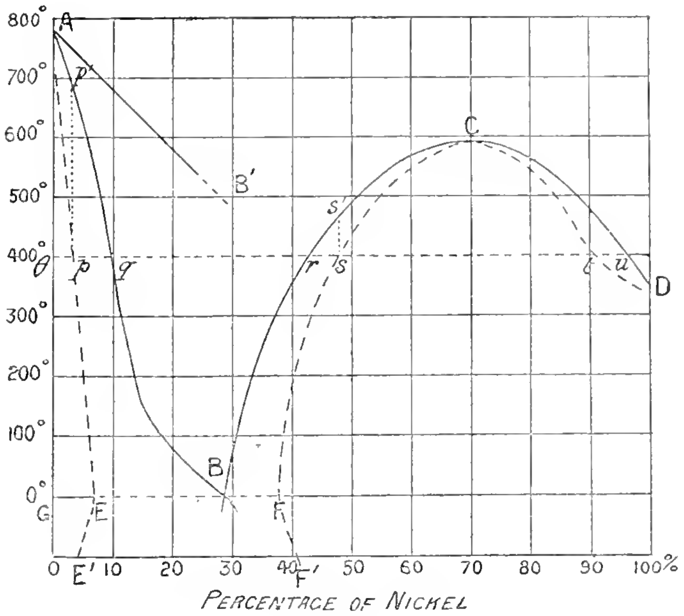


Fig. 23.

converse being true when the transition temperature is raised (*cf.* θt and θu, representing the case in which the transition point is that of nickel raised by addition of iron).

The fundamental ideas represented in the diagram may be summarised as follows:—

(1) When an alloy contains less than GB per cent. of nickel, the crystals which separate first contain less nickel than the remainder of the alloy, and are richer in iron the less the percentage amount of nickel in the material.

(2) When GB per cent. of the nickel is present, crystals of two kinds, one relatively rich and the other relatively poor in nickel, can exist in equilibrium with the (non-magnetic) solution containing GB per cent. of Ni and separate simultaneously when the temperature corresponding to GEF is reached.

(3) When the percentage of nickel exceeds GB the crystals which first form on cooling are those of the second type, relatively rich in nickel.

(1*a*) The ultimate state, at the temperature represented by GEF, of an alloy containing less than GB per cent. of nickel is different according as the percentage of nickel present is less than or exceeds GE.

If the alloy contains less than GE per cent. of Ni, it will be crystallised completely before GEF is reached, and will contain crystals of one type only, of which the percentage composition will be the same as that of the originally uncrystallised alloy. The alloy will be homogeneous at the temperature represented by GEF.

If the alloy contains more than GE per cent. of nickel, the percentage of Ni in the crystals will increase, at the same time that the total amount increases, until the eutectic temperature is reached. Here the last of the solid solution (containing GB per cent. of Ni) crystallises, but partly in the form of crystals weak in nickel (containing GE per cent.) and partly in the form of crystals stronger in nickel (containing GF per cent.). Hence any alloy containing more than GE per cent. and less than GB per cent. of Ni will be heterogeneous when completely crystallised at the eutectic temperature.

(2*a*) When the alloy contains GB per cent. of Ni, the material will be, when completely crystallised at the eutectic temperature, a mixture in definite proportions of the two types of crystals, one relatively rich and the other relatively poor in nickel.

(3*a*) The ultimate state, at the eutectic temperature, of an alloy containing more than GB per cent. of nickel will be different according as the percentage of nickel is less than or exceeds GF.

If the alloy contains less than GF per cent. of Ni, the eutectic temperature will be reached before the whole of the solution has crystallised. The final crystals will form from a solid solution containing GB per cent. of nickel, and will be a mixture of the two types containing respectively GE and GF per cent. of nickel. When completely crystallised at the eutectic temperature the alloy will be heterogeneous.

If the alloy contains more than GF per cent. of nickel, it will be crystallised completely before the eutectic temperature is reached, and will contain crystals of one type only, of which the percentage composition will be the same as that of the originally uncrystallised alloy. The alloy will be homogeneous at the eutectic temperature.

In all the cases described above, with the exception of that in which the alloy contains GB per cent. of nickel, the composition of the crystals changes continuously during the process of cooling to the eutectic temperature. When the percentage of Ni is less than GB the crystals become continuously richer in nickel; when the percentage is greater (but less than that represented by C) they become continuously poorer. If, however, the alloy contains the percentage of nickel represented by the dystectic point C, the crystals and the solid solution from which they form will be of the same composition from the beginning to the end of the crystallising process.

§ 3. As stated above, the crystallised material is homogeneous at the eutectic temperature if the alloy contains originally less than GE or more than GF per cent. of nickel. This result need not apply, however, to lower temperatures if the equilibrium curves below the eutectic temperature are (as they may be by analogy with fluid solutions) of the form represented qualitatively by EE′ and FF′ respectively. Under such circumstances alloys containing slightly less than GE per cent. or slightly more than GF per cent. of Ni might become heterogeneous at temperatures not very far below the eutectic temperature.

§ 4. There are various experimental data which are explained by the views above summarised of the relation between the structure and temperature of a nickel iron alloy of given composition.

That the formation of crystals of varying composition can occur in an alloy has been proved by direct experiment, and that this crystallisation occurs in a way analogous to that in which it takes place in liquid solutions has also been shown.

The distribution in space of the chemical constituents of a homogeneous alloy is analogous to that which exists in a solution, and the redistribution on crystallisation is the same phenomenon in each case, although the conditions under which the redistribution occurs in a fluid medium must be different from those in which it takes place when the medium is solid. Experiment has shown, however, that interdiffusion of metals can take place even at low temperatures, and hence to postulate the interdiffusion of the nickel and iron, as in the above theory, does not involve the introduction of an *ad hoc* hypothesis.

The theory involves the result that in any nickel-iron alloy—assuming the magnetisability to be a function of the state of crystallisation—the magnetism will not appear and disappear at one definite temperature. Thus in alloys containing θp, θs per cent. of nickel, crystallisation will begin at temperatures corresponding to p', s' respectively, and will not be complete until temperatures corresponding to p, s are reached.

Hence over the range of temperature represented by $p'p$ in the one case and by $s's$ in the other the amount of magnetic material will be increasing. In only one alloy, viz., that corresponding with C, in which the composition of the crystals is the same as that of the solid solution, will it be possible for the magnetism to disappear or reappear completely at one temperature. The data given by OSMOND (*loc. cit.)* are qualitatively in agreement with this deduction. The curves which he gives show that in the alloy containing 76·75 per cent. of nickel the magnetism reaches its full value very rapidly, after the temperature of reappearance is reached, just as it does in pure iron. It is further clear on inspection of the curves ('Rev. Gén.,' vol. XIV., pp. 868 and 869, 1903), that the range over which the permeability reappears becomes wider as the percentage of nickel increases from A or diminishes from C. Similarly with percentages above C, the range over which the magnetism reappears at first widens, but, as D is approached, again becomes restricted (*cf.* also Section VI., § 8, p. 88).

§ 5. The connection between permeability and the state of crystallisation is directly suggested in an experiment by GUILLAUME ('Comptes Rendus,' vol. 134, p. 596). A non-magnetic specimen of nickel steel, part of the surface of which was polished, was cooled down, with the result that visible crystals were developed and that the material become magnetic. According to GUILLAUME ('Journ. Iron and Steel Inst.,' vol. II., p. 297, 1905), the first observation of this kind was made by OSMOND.

By observation of the changes of volume (which are accompanied by the appearance of magnetism) in certain nickel-iron alloys, GUILLAUME has shown (see 'Rev. Gén.,' 1903, *loc. cit.*) that these changes agree quantitatively with the view that the presence of the nickel merely alters the temperature at which the transition of the iron in the alloy, from the non-magnetic to the magnetic state, takes place. The simplest interpretation of his results is that the nature of the change is the same in all the alloys, while the temperature at which the change begins, and the rate at which it proceeds, depends upon the percentage of nickel. The experiments are necessarily comparatively restricted and the argument is based partly upon a process of extrapolation.

It is known that there is no appreciable change in the density of nickel when it passes from the non-magnetic to the magnetic state, and hence the metrological method used by GUILLAUME (depending upon observation of the change in length of a bar of the nickel iron) affords no information concerning the changes that may take place in the nickel during the crystallisation of the iron by which it is accompanied in the alloy.

§ 6. The marked change in the magnetic properties of nickel-iron alloys when the percentage of nickel passes through a value between 25 and 30 is shown clearly in the data given by HOPKINSON (' Roy. Soc. Proc.,' vol. 48, 1890), and confirmed by the work of subsequent observers (*cf.*, *e.g.*, BARRETT, ' Trans. Roy. Soc. Dubl.,' 1902–1905).

The change in the magnetic properties corresponds closely with a well-marked change in crystalline structure which has been studied in detail by GUILLET (' Metallographist,' vol. 6, 1903). This change takes place, according to GUILLET, when the percentage of nickel is 27, if the percentage of carbon in the alloy is small.

Other data of a similar kind might be cited in support of the hypothesis that the permeability is intimately related to the crystalline structure, and of the deduction therefrom that observation of the permeability variation may be valuable as a means of tracing continuously variations in the state of crystallisation of the material.

It will be seen that the experiments described in this paper bear directly upon this point; but before considering the evidence of the validity of the theory of solid solutions, which they convey, it seems well to indicate how, as it appears to me, the value of the theory as an explanatory hypothesis can be exhibited by consideration of certain data already known.

The method of presentation of the facts enumerated and discussed in §§ 7–17, below, was suggested to me by a consideration of those thermomagnetic data of Section IV. which are discussed in Section VII.

§ 7. As already stated, the positions of the dotted curves AEFCD in fig. 23 above are in the first instance purely qualitative. The values of GE and GF, for example, which represent the compositions of the two components of the supposed eutectic are not known from direct experiment upon artificial alloys; but a study of the structure of nickel-iron alloys of natural origin ("meteoric" and "terrestrial") strongly supports the view that the equilibrium curves are of the general form given in the figure.

The results of the chemical analysis of meteorites (see, *e.g.*, COHEN, ' Meteoritenkunde,' 1894–1903) show that the amount of nickel (together with cobalt) found in meteoric iron is seldom less than 6 per cent. or more than 11 per cent. It is probably for this reason, as will be seen, that Widmanstätten figures are usually regarded as a characteristic of meteoric iron. But while the occurrence of *large* and almost perfectly symmetrical figures may, in the present state of knowledge (since the means of producing such figures artificially has not yet been discovered), be regarded as a sign of "meteoric" origin, yet the absence of such figures does not prove that the iron is not meteoric. There is a considerable number of specimens of iron which, judged by their mode of occurrence and general appearance alone, would be accepted as of similar origin to those classed as meteoric, but of which the origin, on account of the absence of the Widmanstätten figures, is regarded as doubtful. In each of these doubtful cases the percentage of nickel is either appreciably lower than 6 per cent. or appreciably higher than 11 per cent., and the composition is in consequence described sometimes as "anomalous." But it is clear that this point of view is conventional.

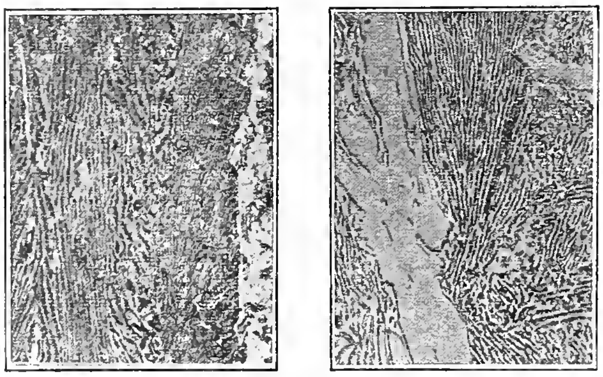
The essential fact is that no nickel-iron alloy, meteoric or terrestrial, is known which gives Widmanstätten figures when the percentage of nickel, in the portion of the material showing the figures, is less than about 6 or more than about 15. Neither of these limits has been fixed precisely, because the structure of an alloy which gives the figures is heterogeneous and the amount of the meteorite used for the analysis is generally small (*cf.* COHEN, I., p. 86).

§ 8. Numerous analyses are available of meteoric irons, poor in nickel, which are practically homogeneous (COHEN, I., p. 97). From these it is seen that the percentage of nickel may be as high as 7 per cent. without occurrence of Widmanstätten figures. Moreover, the crystalline characteristics and other physical properties of "hexahedral" iron (the commonest of the homogeneous types) are practically identical with those of the kamacite of octahedral iron (COHEN, I., p. 85), and, finally, although such iron may contain only 4 per cent. of nickel or less (*cf.* COHEN and BREZINA, 'Akad. Sitzungsb. Wien,' vol. 113, 1904; MOISSAN, 'Comptes Rendus,' vol. 139, p. 773, 1904), those specimens richest in nickel contain practically the same percentage of nickel as the kamacite of octahedral iron. Hence it seems clear that the percentage of nickel can reach some value between 6 and 7 without occurrence of heterogeneous crystallisation in the material from which the meteorite is formed; and that when the amount exceeds this value, the whole of the material cannot crystallise as kamacite. Another alloy richer in nickel (taenite) then makes its appearance, and the production of Widmanstätten figures by etching becomes possible.

At first, when the percentage of nickel only slightly exceeds 7, the structure is relatively coarse. The layers of less nickeliferous alloy (kamacite) are broad and the thin lamellæ of the alloy richer in nickel (taenite) which border the layers of kamacite are sometimes absent. But as the percentage of nickel rises, the kamacite layers become narrower and the layers of taenite more abundant. The kamacite is gradually displaced from its position of predominance and the figures eventually become too fine to be visible except when highly magnified (COHEN, I., pp. 100, 101) (*cf.* Section VII., § 15, p. 103).

§ 9. Data are not available by which to decide the question whether there is a definite percentage of nickel at which the Widmanstätten figures disappear. Modern methods of micrographic analyses have not yet been applied to the material at disposal.

Of particular interest, however, in connection with the theory of solid solution is the San Cristobal meteorite. It contains about 26·5 per cent. of nickel (Cohen, 'Sitzungsb. Akad. Wiss., Berlin,' p. 608, 1898), and this, as will be seen from the previous diagram (fig. 23, p. 67), is approximately the percentage contained by the supposed eutectic corresponding to the point B of the diagram. The structure of this meteorite is described by Cohen (*loc. cit.*), and also, more recently, by Brezina (Wien, 'Denkschr. Akad. d. Wiss., math.-naturw. Classe,' vol. 78, p. 638, 1905).* In the photograph given by the latter (Plate II., fig. 12), representing a portion of the meteorite magnified 23 times, the left half of the field shows a remarkable resemblance in structure to the eutectic of iron-carbon alloys of the type known as *lamellar pearlite.* This resemblance is shown in the annexed figure, in which are placed side by side a portion of Brezina's figure and of one given by Osmond ('Microscopic Analysis ot Metals,' p. 85. Compare also 'Roberts-Austen Reports, Alloys Research Committee,' 1899 and 1904).



San Cristobal Meteorite.
(Brezina.)
(?) contains eutectic
percentage of nickel.

Lamellar Pearlite.
(Osmond.)
Contains the eutectic
percentage of carbon.

× 23. × 1000.

Fig. 24.

§ 10. The present state of knowledge concerning the general structure of nickel-iron alloys of natural origin (omitting those in which carbon, phosphorus, and other elements are present in considerable quantity) can be summarised as follows:—

(1) Meteoric iron is, in general, homogeneous when it contains less than 7 per cent. of nickel. (2) It is heterogeneous when the percentage of nickel lies between 7 and 14. (3) It becomes practically homogeneous again when the percentage of nickel exceeds some value, apparently between 15 and 35 per cent., which could possibly be fixed by further careful microscopic investigation.

It is clear that these facts can be interpreted if we assume that the taenite (thin layers of nickeliferous material), which appears when the percentage of nickel exceeds 7, is a eutectic consisting of (1) "mixed crystals" containing about 7 per cent. of Ni, and (2) "mixed crystals" containing the considerably higher percentage of Ni corresponding to that at which the structure of the alloy again becomes homogeneous.

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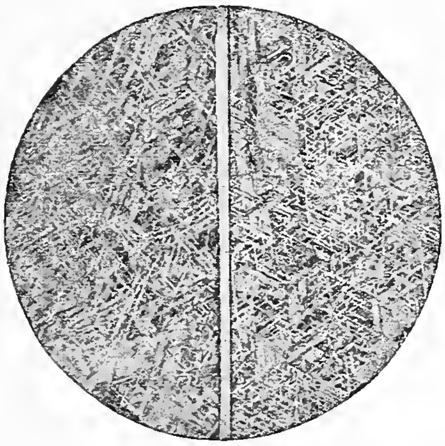
* I am indebted to Mr. L. Fletcher, F.R.S., for drawing my attention to this paper.

§ 11. With respect to the evidence that taenite is a eutectic there is to be noted, first, its mode of occurrence and distribution (already indicated), next, its microscopic and chemical characteristics, and, in conclusion, as will be seen, the magnetic properties of the meteoric iron in which it occurs.

In connection with the distribution of taenite mention should be made of a very striking photograph given by ARNOLD and McWILLIAM ('Nature,' vol. 71, p. 32, 1904. Similar photographs have been given by OSMOND, 'Annales des Mines,' vol. 17, Plate III., 1900—and by others). From this photograph it is evident that a steel containing about 0·4 per cent. of carbon gave, on comparatively rapid cooling after casting, a micrographic structure practically identical in form with that of octahedral meteorites. The two constituents "ferrite" and "pearlite" are distributed in the same way as the "kamacite" and "taenite" in the meteoric iron.

To indicate the degree of similarity, there are placed side by side in the accompanying figure the photograph given in 'Nature' (*loc. cit.*) and a reduced copy of the photograph given by COHEN and BREZINA ('Structur der Meteoreisen,' Plate X., fig. 3) of a specimen of meteoric iron (Tazewell meteorite) containing between 12 and 15 per cent. of nickel.



Cast Steel.
× 22 diameters.

0·4 per cent. Carbon.
Ferrite (light).
Pearlite (dark).

Meteoric Iron.
× 2 diameters.

13 per cent. nickel (approx.).
Kamacite (light).
Taenite (dark).

Fig. 25.

In the one photograph the darker constituent is pearlite (ARNOLD and McWILLIAM, *loc. cit.*) and in the other taenite (COHEN and BREZINA, Erklärung der Tafeln, *loc. cit.*). In the one the constituent of lighter colour is ferrite, and in the other kamacite. The section is cut parallel to an octahedral face in the meteoric iron, but the plane of section is evidently slightly inclined to an octahedral face in the steel.

Now a reference to the equilibrium curves for carbon-iron alloys shows that when a 0·4 per cent. carbon steel cools from a temperature above 780° C., ferrite will form in gradually increasing amount, in the state α from the state γ, until the eutectic temperature (690° C.) is reached. At this temperature the remainder of the iron will recrystallise as pearlite, a eutectic mixture of ferrite and cementite.

In the same way, by hypothesis, when a nickel-iron alloy containing, say, 10 per cent.

of Ni cools from a temperature above 700° C., kamacite will form in gradually increasing amount until the eutectic temperature (below 100° C.) is reached. At this temperature the remainder of the material, containing the percentage of Ni represented by GB (fig. 23, p. 67), will separate as taenite, an intimate mixture of kamacite containing GE per cent. of Ni and of a more nickeliferous alloy containing GF per cent. As will be seen, the extraordinary similarity between the structures of the iron-carbon and iron-nickel alloys above described would follow as a natural consequence of this hypothesis. Hence the way in which taenite is distributed relatively to the kamacite strongly supports the view that taenite is a eutectic.

§ 12. The microscopic characteristics of taenite, when examined under high magnification, are in accord with this view. All observers agree that it is not homogeneous (*cf.* Tschermak, 'Denkschr. Akad. Wiss. Wien,' vol. 31, p. 187, 1871; Osmond, 'Comptes Rendus,' vol. 137, p. 1057, 1903).

§ 13. The chemical analyses of taenite confirm the view that it is not homogeneous. Different analyses of the kamacite of octahedral iron do not vary much among themselves and show that this alloy usually contains between 6 and 7 per cent. of nickel. It is otherwise in the case of taenite. References are given by Cohen (*loc. cit.*, I., p. 102, II., p. 217) to the published analyses of taenite and I have arranged these in three groups in the following table.

Percentage of Ni (Co).	Meteorite.	Observer.	Reference.
13·56	Cosby Creek	Reichenbach	'Pogg. Ann.,' 1861, vol. 114, p. 258.
14·0	Caille	Meunier	'Ann. Chim. et Phys.,' 1869 (4), 17, p. 31.
15·0	Caille	Meunier	'Ann. Chim. et Phys.,' 1869 (4), 17, p. 32.
16·68	Casas Grandes	Tassin	'Proc. U.S. Nat. Mus.,' 1902, 25, p. 73.
19·6	Kenton	Nichols	'Field Columb. Mus.,' 1902, p. 314.
24·65	Welland	Davison	'Amer. Journ. Sci.,' 1891 (3), 42, p. 64.
26·70	Welland	Davison	'Amer. Journ. Sci.,' 1891 (3), 42, p. 64.
25·73	Staunton	Cohen and Weinschenk	'Ann. Nat. Hofm. Wien,' 1891, vol. 6, p. 146.
27·0	Cosby Creek	L. Smith	'Comp. rend.,' 1881, vol. 92, p. 843.
28·41	Magura	Weinschenk	'Ann. Nat. Hofm. Wien,' 1889, vol. 4, p. 97.
29·74	Cranbourne	Flight	'Phil. Trans.,' 1882, p. 888.
30·33	Misteca	Cohen	'Ann. Nat. Hofm. Wien,' 1892, vol. 7, p. 152.
31·54	Cañon Diablo	Florence	'Amer. Journ. Sci.,' 1895 (3), 49, p. 101.
34·00	Medwedewa	Berzelius	'Pogg. Ann.,' 1834, vol. 33, p. 133.
34·46	Wichita	Cohen and Weinschenk	'Ann. Nat. Hofm. Wien,' 1891, vol. 6, p. 155.
34·61	Chupaderos	Manteuffel	'Ann. Nat. Hofm. Wien,' 1892, vol. 7, p. 150.
34·74	Toluca	Cohen and Weinschenk	'Ann. Nat. Hofm. Wien,' 1891, vol. 6, p. 137.
35·66	Cañon Diablo	Fahrenhorst	'Ann. Nat. Hofm. Wien,' 1900, vol. 15, p. 376.
36·96	Glorieta	Cohen and Weinschenk	'Ann. Nat. Hofm. Wien,' 1891, vol. 6, p. 157.
37·31	Bischtübe	Cohen	'Ann. Nat. Hofm. Wien,' 1897, vol. 12, p. 54.
38·13	Youndegin	Fletcher	'Mineral. Mag.,' 1899, 12, p. 174.
48·43	Beaconsfield	Sjöström	'Sitzungsb. Akad. Berlin,' 1897, p. 1041.

§ 14. The earlier data contained in the above table are doubtful, since they represent the results of the first attempts at analysis of taenite. For instance, in some of Meunier's experiments the kamacite and taenite were separated by means of the difference in colour, blue in the one and yellow in the other, produced by superficial oxidation of a powdered sample of the iron. Since careful microscopic examination shows that taenite and kamacite can occur in alternating layers, each not more than a small fraction of a millimetre in thickness, it is clear that such a method of separation cannot be relied upon. The difficulty of completely separating nickel and cobalt from iron by chemical analysis has, moreover, been realised more fully since the date of these experiments.

Of the two later analyses giving a percentage of nickel in taenite less than 20, it is not claimed for the second that it is more than "fairly correct." Only 0·02 gramme of material was used in the analysis, and this amount was obtained by a laborious mechanical selection from the rest of the iron.

With respect to the analysis by Tassin, it is not certain from the description how the separation was effected.

A later analysis by Tassin of a sample of taenite from another meteorite yielded 36 per cent. of nickel ('U.S. National Museum,' vol. 28, p. 215, 1905).

§ 15. In the second group of the table are collected the analyses which give values for the nickel (together with cobalt) content ranging between 25 per cent. and 30 per cent.

In three at least of the seven analyses (those by Davison and Flight respectively) the method of separation was mechanical. No chemical solvent was used. In the paper describing the analysis of the Cosby Creek (Sevier) meteorite no details are given, but the material was apparently picked out of portions of the iron which had been disintegrated by oxidation. It is significant to note that this taenite and that analysed earlier by Reichenbach (and giving 13·56 per cent. of Ni) were obtained from different specimens of the same meteoric iron (see Cohen, I., p. 103). Of the two analyses given by Davison, one refers to the comparatively broad bands of taenite (thickness $\frac{1}{15}$ to $\frac{1}{30}$ millim.), and the second to the narrower bands (thickness about $\frac{1}{100}$ to $\frac{1}{200}$ millim.) picked from the so-called "plessitic" layers of the iron.

With respect to the specimens of taenite in this group, which were separated chemically by the continued action of dilute hydrochloric acid, it is noteworthy in connection with the interpretation which follows below, (1) that the physical properties of the Magura taenite agree closely with those of the plates picked by Flight from the Cranbourne meteorite, and that the iron is described by Weinschenk as soluble with difficulty; (2) that the plates of Staunton taenite were relatively thick and rich in carbon; (3) that the physical properties of the Misteca taenite were intermediate between those of the Staunton taenite and those of several almost carbon-free taenites referred to below.

§ 16. In the third group of the table the percentage of nickel lies, in round numbers, between 35 and 40.

A distinguishing feature of the analyses collected in this group is the length of time during which the solvent action of the acid upon the material was continued. In each case dilute HCl was used of such strength (usually 1 of acid to 10 or 20 parts of water) that the solvent action upon the nickel-rich alloy (taenite) was very slow compared with that upon the nickel-poor alloy (kamacite). The acid was, in each case, frequently renewed, and the action extended over three months in three cases, and over two months in another. One analysis only (Cañon Diablo, Florence) gave a less percentage of nickel than 34, viz. 31·54, and against this must be placed a subsequent analysis of a specimen of the same meteorite performed, purposely with the greatest care as a check upon the first, by FAHRENHORST and giving the value 35·66.

It is important to notice that the total percentage of taenite in the iron varied greatly from one meteorite to another. Thus, for example, COHEN obtained from about 70 grammes of Bischtübe iron enough taenite to enable him to use 0·4 gramme in his analysis; while out of 100 grammes of the Youndegin meteorite FLETCHER obtained less than 0·1 gramme. The Glorieta meteorite was especially rich in taenite (containing apparently more than 10 per cent. of the latter) and was characterised by extremely thin alternating layers of kamacite and taenite. The removal of the kamacite (which was relatively very difficult) left a sponge-like skeleton of taenite, and during the action of the acid it was noticed that plates not more than 0·15 millim. thick sometimes consisted of alternating layers of kamacite and taenite.

Under the circumstances of the analyses, as indicated above, the agreement amongst the numbers obtained by different observers is remarkable, and it seems difficult to avoid the inference that the ultimate residue, after the action of the acid, was in every case the same.

But for the analysis of the Beaconsfield taenite, which is anomalous in more respects than its percentage of nickel (*e.g.*, its specific gravity), the data so far considered agree with the view that the percentage of nickel in the nickel-rich constituent of taenite is not very different from 40.

§ 17. The last point in connection with the chemical data, regarded in this way, is the information they afford concerning the percentage composition of the eutectic as a whole.

If taenite is the eutectic, the action of the acid during long continued treatment of meteoric iron is twofold. In the first place it removes the layers of kamacite adjacent to the taenite, and in the second, when the action is sufficiently long continued, it removes the portion of the eutectic that consists of kamacite from the taenite itself; but *if the taenite can be separated mechanically from the adjacent kamacite and analysed, the percentage of nickel found will be that contained by the eutectic.* In the Welland and Cranbourne meteorites the mechanical isolation of the taenite was undertaken on account of the comparative ease with which it could be performed. The average of the percentages of nickel obtained in this mechanically isolated taenite is approximately 27—almost identical with that obtained in the Cosby Creek taenite, which was probably also separated mechanically. It is remarkable that this percentage should agree so nearly with that suggested by thermomagnetic data to be contained by the eutectic; but the interpretation from the present point of view is obvious.

The chemical data can thus be explained simply if it is assumed that octahedral iron consists of two nickel-iron alloys, one (kamacite) nickel-poor but homogeneous and easily soluble in very dilute hydrochloric acid, the other (taenite) nickel-rich but heterogeneous and consisting of alloys nickel-richer and nickel-poorer, of which the poorer is much the more soluble in the dilute acid.

§ 18. In the classification of the constituents of octahedral iron, proposed originally by Reichenbach, it is usual to include a third constitutent, "plessite." It is distinguished by its mode of occurrence; but, on account of the difficulty of isolation, no complete analysis has been made. Unless the meteorite is comparatively rich in nickel, plessite is not abundant; in many octahedral meteorites it is scarce, and in some it is apparently absent (*cf.* Cohen, *loc. cit.* II., p, 219).

This section of the paper in its original form included a discussion of the nature of plessite and of the point of view advocated by Osmond that plessite is the eutectic; but this discussion, to some extent a digression and involving also the question of nomenclature, is omitted from considerations of space.

§ 19. In discussing the question of the composition of meteoric iron from the point of view of the theory of solution, Osmond suggests that the curve showing the temperature of disappearance of magnetism in the irreversible alloys should be regarded as the true equilibrium curve marking the beginning of crystallisation (accompanied by the appearance of magnetism) in these alloys. On the assumption that the irreversibility would disappear if the cooling were excessively slow, and that the rate of cooling of the meteoric iron may have been such as to satisfy this condition for reversibility, Osmond infers that the eutectic temperature could be as high as 360° C., and also that the compositions of the constituents of the eutectic could be explained from the curves (*cf.* fig. 23, p. 67) if it appeared subsequently (from chemical or other evidence) that the eutectic found in meteorites contained as much as 40 per cent. of nickel and was composed of alloys containing possibly 5 per cent. and 50 per cent. of nickel respectively.

The work on carbon-iron alloys above referred to (Arnold and McWilliam, *loc. cit.*) shows incidentally that although slow cooling *may* be essential to the production of large-scale Widmanstätten figures, this is not the case—as far as mere form is concerned—when the figures are small.

Further, it is doubtful (see below, Section VII., § 15, p. 103) whether infinitely slow cooling would cause crystallisation to proceed in the way which Osmond suggests.

Again, if it cannot be said that the chemical evidence disproves the view that the eutectic contains 40 per cent. of nickel, it can at least be said that there is as much in favour of the view that it contains between 25 and 30 per cent.

It would be unwise to generalise from the thermomagnetic analysis of a single specimen; but, as will be seen below, the Sacramento meteorite certainly possesses a constituent containing between 25 and 30 per cent. of nickel, of which the internal structure is complex and, as seen above, a consideration of the chemical data in detail distinctly supports the view that there is a constituent *in all octahedral meteorites* which contains between 25 and 30 per cent. of nickel and which consists of components unequally attacked by acids.

Finally, the presence of a 25 to 30 per cent. Ni constituent can be explained naturally, on the assumption that it is a eutectic, by means of the already known thermomagnetic properties of nickel-iron alloys; while the existence of a 40 per cent. Ni eutectic requires, for its explanation from the experimental curves, hypothetical extrapolation.

SECTION VI.—AN INTERPRETATION OF THE "IRREVERSIBILITY" OF NICKEL-IRON ALLOYS.

§ 1. From the point of view of the theory of solution, considerable interest attaches to those experiments of the present paper in which the nature of the thermal hysteresis of the nickel-iron alloys is examined.

The qualitative resemblance between the thermal hysteresis in the return of magnetism in nickel-iron alloys and the phenomena of supersaturation has already been commented upon (*cf.*, *e.g.*, GUILLAUME, 'Recherches sur le Nickel et ses Alliages,' 1898).

A comparison of the properties of nickel-steel with those properties of supersaturated solutions recently described by MIERS ('Nature,' August 24, 1905, vol. 72, p. 412) suggests that the analogy is even closer than has appeared hitherto. MIERS finds that a solution of a salt of given strength, saturated at a temperature θ_1, remains supersaturated, when the temperature is lowered, until a definite temperature θ_2 is reached. Throughout the range θ_1 to θ_2, crystallisation will not begin, however long the solution be allowed to stand (if surface evaporation is prevented), unless crystals of the salt are added from without. The value of θ_2, like that of θ_1, depends upon the strength of the solution. If crystals are introduced at temperatures between θ_1 and θ_2, they grow at the expense of the salt in solution; but the growth proceeds slowly even if, in order to facilitate uniform distribution of the salt, the solution is kept stirred.

When, however, the temperature reaches θ_2, a change in the condition of equilibrium of the solution occurs, which is accompanied by spontaneous generation of crystalline nuclei. The solution, saturated at θ_1, may be said to pass from the metastable to the labile state at θ_2. The immediate effect of the formation of the crystalline nuclei is, of course, to reduce the concentration of the salt left in solution. Hence, since the temperature of transition from the metastable to the labile condition decreases when the concentration is diminished, the remaining solution is metastable at the temperature θ_2, and further crystallisation can ensue only in the way already described as characteristic of the metastable state, viz., round the crystalline nuclei formed. It will be assumed for simplicity that any thermal effect accompanying the formation of crystals can be ignored.

If the temperature is kept constant at θ_2, there will be a very slow crystallisation of the salt in solution. The amount taking place will be very small if the time during which the temperature is maintained constant is short—even if, as before, the solution is kept stirred. If the temperature is maintained at θ_2 for a sufficient length of time, crystals will continue to grow round the original nuclei until the amount of salt left in solution is that required to produce a saturated solution at θ_2. If the temperature is now assumed to fall slightly, the solution becomes supersaturated and metastable. Crystallisation will proceed slowly round the crystals already formed until the solution again becomes saturated, and will then cease. Hence extremely slow cooling from the temperature θ_2 at which the labile condition first appears will be such as to favour the growth of the largest and most symmetrical crystals it is possible to obtain.

If, however, the rate of fall of temperature below θ_2 is rapid compared with that just contemplated, it is easy to see that the process of crystallisation will be different. The temperature will fall below θ_2 before the solution has deposited enough crystals to become saturated at that temperature. It is still supersaturated and, if the amount of crystallisation round the nuclei, since the advent of the labile condition at θ_2, has been small, it will pass almost immediately from the metastable to the labile state. A fresh deposition of crystalline nuclei will then ensue. This process will be repeated again and again as the temperature falls—the growth round each set of nuclei being a very slow process will not proceed far before, by reduction of temperature, the solution has again reached the labile condition. Hence comparatively rapid cooling will cause the growth of a succession of sets of small crystals.

An important deduction (of which the significance in the supposed analogous case of solid solution will be seen below) from the behaviour during comparatively rapid cooling, as set out above, is that at any temperature below θ_2 the amount of crystallisation will reach, practically at once, a value which will not increase appreciably until the temperature suffers a further fall. The rate of growth round the nuclei will be so small compared with the rate of formation of the nuclei themselves that the amount of crystallisation at a given temperature will appear to be approximately a single-valued function of the temperature.

Again, for the purposes of the analogy which it is sought to develop between a crystallising solution and cooling nickel-steel, suppose that the comparatively rapid cooling below θ_2 is interrupted and that the temperature of the mixture of solution and crystals is raised. The crystals will not begin to go into solution again at once, for the solution surrounding them is already supersaturated. They will not begin to re-dissolve until the temperature is attained at which the solution is saturated, and this temperature will be higher in proportion as the temperature from which the reheating begins is nearer θ_2. (It is, of course, supposed throughout that the salt is one of which the solubility increases with the temperature.) Hence, if the temperature is subject to variation between that at which the cooling was interrupted and that at which the solution ceases to be supersaturated, there will be no solution of the crystals formed during the first cooling from above θ_1.

On the other hand, if the temperature is kept constant at any value between the limits in question, there will be a slow growth of crystals around those already formed and the concentration of the solution will approach slowly, from near the crystals outwards, to that corresponding with saturation at the temperature considered.

Further, when the reasons why the rate of growth round the nuclei is slow are considered, it is seen that the alternation of temperature between limits θ'_2 and θ'_1 (where $\theta'_2 > \theta_2$ and $\theta'_1 < \theta_1$) will cause the growth to occur more rapidly than if the temperature were kept constant at θ'_2. The salt crystallises round the nuclei because at the temperature θ_2' the solution in contact with them is supersaturated. By removal of the salt this solution approaches the normal saturation strength at θ'_2, and further crystallisation does not occur until the concentration loss is made good by the diffusion of salt inwards from the more concentrated layers of solution further away from the crystals. Increase of temperature will increase this rate of diffusion and hence, also, the rate of crystal growth. The effect of increase of temperature will be most pronounced at first because the concentration gradient in the solution will have then its maximum value—the crystals being then surrounded by an extremely thin layer of solution saturated at θ'_2, immediately beyond which is the supersaturated solution. At each alternation of temperature the distance over which the concentration varies between saturation at θ'_2 and that of the main bulk of supersaturated solution will become larger and the concentration gradient will consequently become smaller. Hence each successive heating to θ'_1 will be accompanied by the approach of a smaller amount of crystallisable material, to the crystallising nucleus, than the last, assuming each reheating to occupy about the same length of time as the one preceding it. Effects of the kind here contemplated will be most pronounced in solutions of which the viscosity is not only large, but subject to rapid decrease with rise of temperature. They may be represented qualitatively by a diagram, such as that given below (fig. 26, I.), in which the ordinates represent the amount of crystals present in contact with the solution and the abscissæ are temperatures.

It is assumed that an amount of crystals, represented by OA, is present originally in contact with a solution saturated at θ_0, and that when the solution and crystals are heated—the solution being allowed to become saturated at any temperature—the amount of crystals present gradually diminishes, following the upper curve ABC. At θ_1 all the crystals have dissolved, and above this temperature the solution is unsaturated. When the solution is allowed to cool, crystals reappear at θ_2 and, if the cooling continues at such a rate that there is no appreciable growth of crystals except by successive deposits of nuclei, the amount of crystals present at any temperature below θ_2 will be represented diagrammatically by the lower curve C′B′A′.

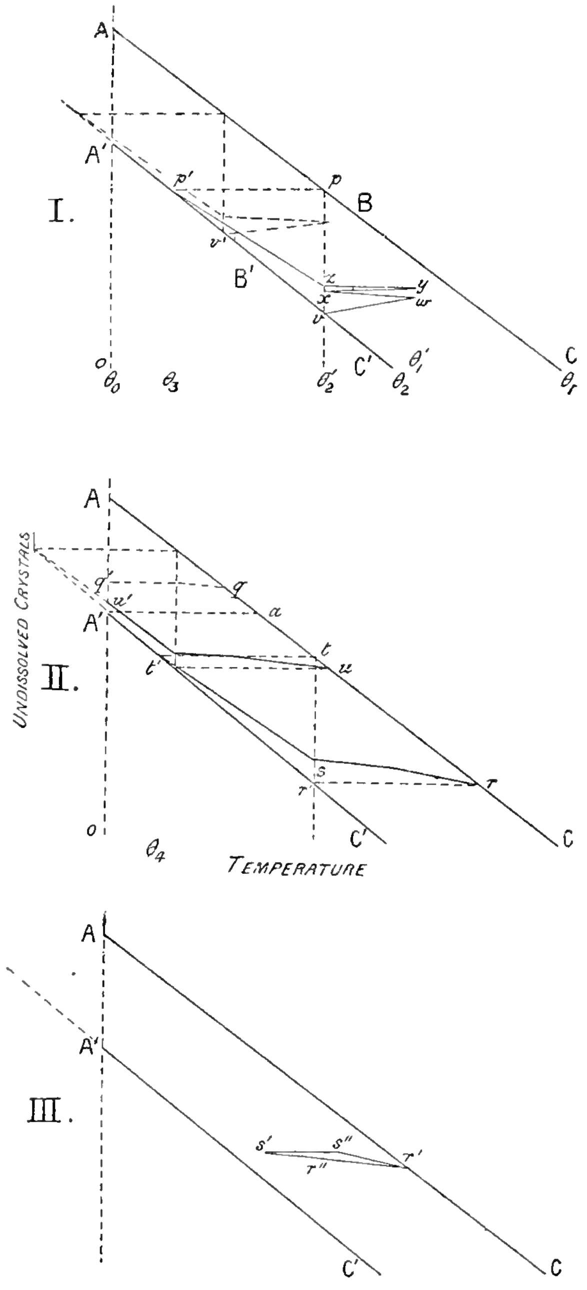


Fig. 26.

If the cooling is interrupted at θ'_2, and the system is re-heated to θ'_1, the amount of crystals present may increase as represented by the curve *vw*. This will not be, in general, a straight line, but a curve of which the slope will vary in a way depending upon the relative magnitudes of the effects of the decrease in the concentration gradient due to deposition and of the increase of the rate of diffusion due to rise of temperature. During cooling from θ'_1 to θ'_2, the growth is represented by the curve *wx*, which is flat compared with *vw*, because the rate of diffusion gets less as the temperature falls. The next curve *xy* may be steeper than *wx*; but the succeeding element *yz* will be flatter. Finally, on account of the continuous decrease in the gradient, crystallisation will proceed so slowly that alternation of temperature between θ'_2 and θ'_1 will be without appreciable effect upon its amount.

Assuming the effect of alternations of temperature carried out comparatively rapidly to be represented by *vwxyz*, the effect of allowing the material to cool below θ'_2 may now be considered. With the exception of the layers surrounding the crystals, the solution will have the same concentration as it possessed when the cooling was first interrupted at θ'_2. It is metastable at θ'_2, but a small lowering of temperature is sufficient to reduce it to the labile condition. Hence crystallisation will begin at θ'_2, and will continue at lower temperatures in this solution exactly as in the case of uninterrupted cooling. Through *p*, the point in which the ordinate at θ'_2 cuts the curve ABC, let *pp'* be drawn parallel to the axis of temperatures and cutting the curve A′B′C′ in *p'*. Then below the temperature corresponding to *p'* (θ_3) the crystallisation curve will coincide with the corresponding part of A′B′C′; between θ'_2 and θ_3 the curve will follow a course represented diagrammatically by *zp'*. This follows because, by hypothesis, the process represented by *vwxyz* caused the strength of the solution round the crystals to become practically equal to the saturation value at θ'_2. From the curves ABC and A′B′C′ it is seen that a solution of this strength does not pass into the labile condition until the temperature θ_3 is reached. Hence there is no further deposition of nuclei from this solution until θ_3 is reached. Further, a solution labile at θ'_2 deposits crystals during cooling at such a rate that it also is labile at θ_3. Hence both the solution which lost salt by deposition round crystals already present and that which lost salt by the continuous formation of nuclei reach θ_3 in the labile condition, and thus, at the end of the process represented by *vwxyzp'*, there will be practically the same amount of labile solution remaining as after uninterrupted cooling along C′B′*p'*. All the solution is again labile at θ_3, and the curves of interrupted and uninterrupted cooling will coincide below this temperature. From the figure (26, I.) it is clear that if the cooling is first interrupted at some temperature lower than θ'_2, like that corresponding with *v'*, the solution round the crystals present, originally, at *v'* may still be metastable when the temperature θ_0 is reached.

Other effects of thermal treatment may be exhibited diagrammatically in a similar way. Thus, to consider the possible effects of interrupted heating following the saturation curve ABC, suppose first that the heating is discontinued before the temperature reaches the value corresponding to the line A′*a* (*e.g.*, at *q*, fig. 26, II.), *i.e.*, before the solution is concentrated enough to become labile, during cooling, at θ_0. Then it is clear that no crystallisation by formation of nuclei will occur during subsequent cooling to θ_0. The crystal growth during cooling, which can occur only round crystals already present, may be represented by the curve qq'.

Next suppose that the heating is first interrupted at some temperature above that represented by a. In this case the strength of the solution is such that on cooling it will become labile before θ_0 is reached. Let r be the point at which the heating is interrupted. Crystals will grow round those already present comparatively rapidly at first, on account of the relatively high concentration gradient and temperature, but the rate of growth will diminish subsequently, because the temperature effect and the effect of the gradient now conspire to retard it. When the temperature reaches the value corresponding to the ordinate $r't$ the supersaturated solution at a distance from the crystals will pass into the labile state, and the formation of nuclei within it will begin. The solution in the immediate neighbourhood of the crystals, being more dilute, will still be metastable, and the last portion of it—that corresponding to saturation at the temperature represented by r'—will not become labile until the temperature θ_4 (represented by t', fig. 26, II.) is reached. At θ_4 all the solution will be in labile equilibrium, and the growth of crystals subsequently will be along C′B′A′. (For the sake of simplicity it has been tacitly assumed that crystallisation round crystals is inappreciable below the point s.)

It is easy to see that if the heating along ABC is interrupted at some point between q and r, such as u, the solution round the crystals will not become labile until some temperature lower than θ_0 is reached.

Finally, consider the case in which the cooling from the curve ABC is interrupted before any of the solution has reached the labile state and the system is reheated. Crystals will grow during the cooling round those present, as already described. When the reheating begins, assuming the solution round the crystals to be still supersaturated, crystals may continue to grow, but, obviously, before the outer curve ABC is reached the temperature will reach a value at which the solution round the crystals is not supersaturated. Beyond this temperature the crystals will begin to re-dissolve and the solution round the crystals will become saturated at the expense of the crystals which were deposited from it during cooling. When the temperature from which the cooling began is reached, practically all the solution will again be saturated at this temperature, and the result of further rise of temperature will be that the crystals will dissolve, following the curve ABC. If the zone in which loss of salt by the solution takes place during cooling is of considerable extent, there will be a perceptible lag in the return of the state in which all the solution is saturated. In such a case the temperature at which the heating was first interrupted will be reached before the whole solution is saturated again at this temperature, and the amount of crystallisation may therefore, for some degrees above this temperature, exceed that corresponding to the saturation curve ABC.

These conclusions rest upon the assumption, which is apparently justified by the experiments of MIERS (*loc. cit.*), that the temperature at which a supersaturated solution becomes labile is a single-valued function of its concentration. It remains to show how many of the results described in Section IV. can be explained on the assumption that crystallisation occurs in nickel steel from a solid solution, in accordance with a similar law.

§ 2. The irreversible phenomena discovered by HOPKINSON can be interpreted at once in terms of the theory outlined above. Thus, whilst magnetism is disappearing during heating, magnetic crystals are, by hypothesis, dissolving in solid solution, and, finally, when all the crystals have disappeared, the material consists of a solid solution only. It is a homogeneous mixture, of which the constituents may be crystalline, but are not magnetic. Further, just as in a mixture of crystals and water, the temperature at which the last of the crystals dissolve rises when the relative amount of crystals originally present is increased, so the temperature of the disappearance of magnetism, in a mixture of iron crystals and nickel, rises when the percentage amount of iron present increases.

When the magnetism has just disappeared, a saturated solid solution remains. If this is allowed to cool it becomes supersaturated and metastable, but eventually it becomes labile. The temperature of lability, at which spontaneous recrystallisation begins, is definite and depends upon the relative amounts of nickel and iron present in the material. It decreases as the percentage of nickel in the alloy increases, just as the temperature at which lability is reached in a supersaturated salt solution decreases as the percentage of water which it contains increases.

Thus, qualitatively, the manner of disappearance and reappearance of magnetism in nickel-iron alloys corresponds with that of disappearance and reappearance of crystals in fluid solution.

§ 3. The applicability to the case of solid solutions of the fundamental hypothesis discussed in § 1 with respect to fluid solutions seems to receive remarkable confirmation from the experiments already described. The general characteristics of the thermomagnetic curves and the quantitative relations between them, when a numerical comparison can be made, are in accord with the theory.

The changes in the alloy when heated will differ slightly from those in the hypothetical case of an aqueous salt solution considered above. They will correspond more nearly with those which would occur in a crystallised salt which can go into solution in its own water of crystallisation. Referring to fig. 27, IV., the amount of crystalline material will remain constant (following the horizontal line) until a temperature is reached represented qualitatively by B. Gradual solution of the crystals will then begin and will continue until, at the point C, they have disappeared.

If the percentage of nickel in the alloy is less than that contained by the eutectic, the changes that take place in the material in the region BC will be (according to the theory of mixed crystals) as follows :—

Considering a small element of the material at first magnetically crystalline, when the temperature is slightly above B, a small quantity will change its state. There will be a redistribution of the components chemically as well as physically, since the composition of the crystals is different from that of the solution. The small quantity of solid solution first formed will be richer in nickel than the mixed crystals which remain. A larger fraction of the total amount of nickel than of the total amount of iron will go into solution.

But as the relative amount of the solution increases, the percentage amount of nickel it contains will diminish, until, finally, when the last of the crystals disappear, the composition of the solid solution will be the same as that of the original crystallised material.

During recrystallisation the reverse process will occur. The crystals first formed will be relatively weak in nickel, but as their amount increases so also will the percentage of nickel they contain. A larger fraction of the iron than of the nickel goes into the crystals, however, and the solution gets richer in nickel also, although it diminishes in amount.

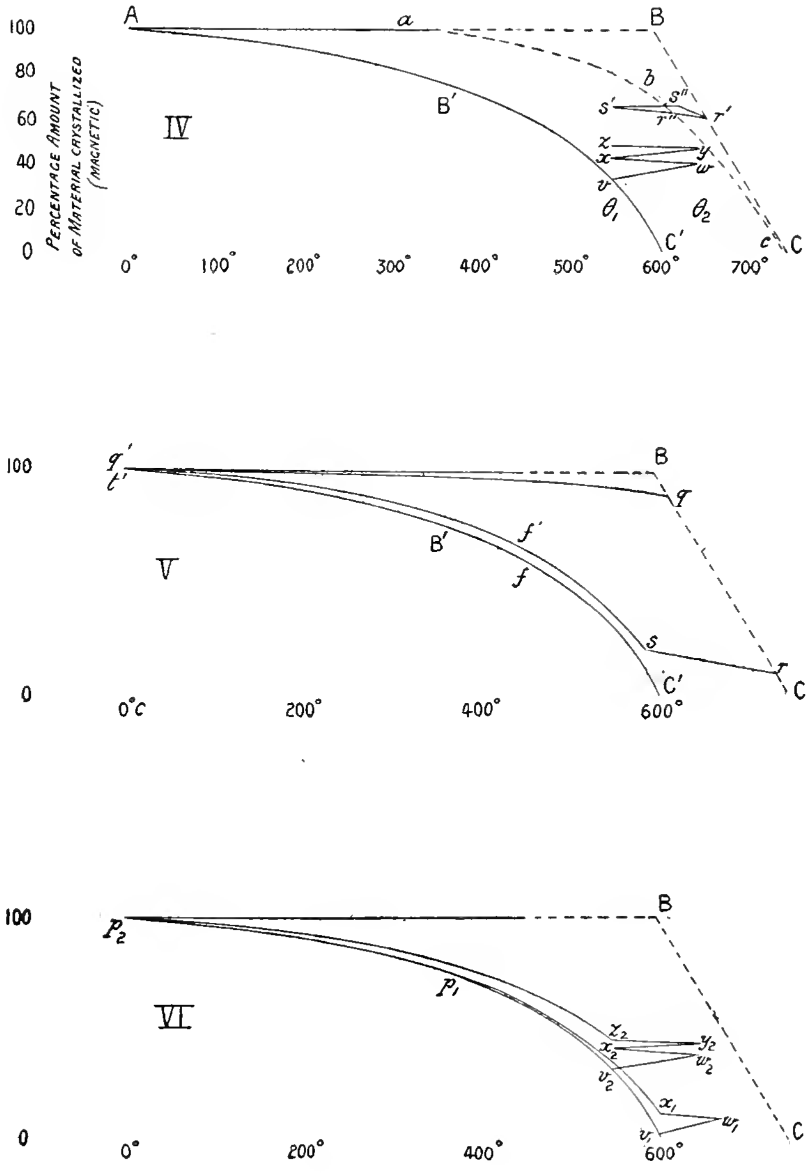


Fig. 27.

§ 4. To show how closely the permeability measurements agree with the view that the phenomena assumed above really occur, consider first fig. 27, IV.

Assume that the nickel-iron alloy contains about 6·5 per cent. of nickel. Crystals will begin to disappear at a temperature which has not yet been accurately fixed. Their solution will be complete at a temperature not far from 750° C.

The change may be represented qualitatively by the curve *a*BC (the ordinate giving the percentage of the material that is still crystalline at the temperature corresponding to the abscissa), although the curve for extremely gradual heating is more probably of the form represented diagrammatically by *abc*.

The curve of crystallisation during cooling can be calculated roughly from the data at disposal. Thus, at any temperature θ, the percentage of nickel in the labile solid solution is known approximately, since it is, by hypothesis, the same as the total percentage of nickel contained by that alloy in which magnetism reappears at θ.

It may be assumed as a first approximation from the experimental data that θ decreases linearly from $\theta = 780°$ C. when the percentage of nickel is negligible to $\theta = 0°$ C. when the percentage of nickel is 27, *i.e.*, that the curve AB of fig. 23 on p. 67 is approximately a straight line.

The percentage of nickel in the crystals in equilibrium with the labile solid solution in question is θp (fig. 23), θq being the percentage of nickel in the solution. Again assume, as a first approximation, that the curve AE showing the variation in the percentage composition of the crystals is a straight line. For reasons already given, suppose that E corresponds roughly to 6·5 per cent. of nickel.

If a is the total percentage amount of Ni in the alloy, and if x is the percentage amount of the alloy which is crystalline at the temperature θ, we have

$$\frac{\theta p}{100} x + \frac{\theta q}{100} (100 - x) = a,$$

from which, assuming that θp and θq can be calculated roughly as above, it is possible to find the value of x for any value of θ.

The curve C′B′A of fig. 27, IV., is plotted from numbers calculated in this way for $a = 6{\cdot}5$. It is assumed that the rate of cooling is sufficiently slow to ensure that all the crystals at any temperature contain the same percentage of nickel.

§ 5. The first conclusion from the curve C′B′A is that, in an alloy containing 6·5 per cent. of nickel, the amount of magnetic iron will increase rapidly at first as the temperature falls below 600° C., and then more gradually. The final portions of the alloy will become magnetic very slowly, and the return to the magnetic state of all the iron in the alloy will not be complete until the temperature is below the ordinary temperature of the air. This accounts for the fact, carefully examined in the first experiments with the meteoric iron (1st winding) and corroborated subsequently, that the permeability during cooling, *e.g.*, at 550° C., is considerably below that shown at the same temperature during reheating from 15° C. The fact is less obvious in the case of the artificial nickel steel. Thus, considering only the curves given by HOPKINSON and the corresponding curves of fig. 18, it would appear that all the iron had become magnetic when, during cooling, the temperature had fallen to about 550° C. But the later measurements show that the material is not in a state of final equilibrium at temperatures below 600° C. until it has undergone successive alternations between that temperature and 15° C., and that, when this state is considered, the behaviour of the steel is analogous to that of the meteoric iron (*cf.* § 12 below, p. 92).

§ 6. If the cooling is interrupted at some temperature below that at which magnetism appears and if the temperature is then varied between this and some higher temperature (*cf.* fig. 26, I.), the amount of magnetic iron should increase at first relatively rapidly and finally very slowly, as already explained. The slope of vw (figs. 26, I., and 27, IV.) should be greater than that of xy, and that of wx should exceed that of yz. In the same way the permeability change corresponding to vw should exceed that corresponding to xy, and that corresponding to wx should be greater than that corresponding to yz. If diffusion can only take place slowly, the increase in permeability will become imperceptible after a few alternations; xy and yz will be practically horizontal, and the temperature coefficient of permeability between the temperatures θ_1 and θ_2 (fig. 27, IV.) will become practically identical with that observed when all the iron is magnetic.

Examination of the data given in the tables shows that after the first alternation between given temperature limits in the meteoric iron and in the nickel steel, the change produced by subsequent alternations (during the time occupied by the experiments) is practically inappreciable, *i.e.*, xy, yz, &c., are practically superposed. An example of this is given in the data 30 to 34, meteoric iron, 2nd winding, fig. 11. A similarly rapid approach to a steady state is shown in the data 82 to 86, fig. 13.

Besides these examples of the process $vwxyz$, there are also numerous examples of the process vwx in the tables, which incidentally lead to the conclusion that if y and z had been observed in these cases the results would have been the same as in the experiments above mentioned. For the temperature coefficient of permeability over the range represented by wx has, within the limits of experimental error, in each case reached almost the same value as that over the same range when the material is fully magnetic. This is seen by comparing Experiments 51 and 52, 1st winding, with 8 and 9, and also Experiments 27 and 28, 75 and 76, 79 and 80, &c., 2nd winding, with 92 and 93. Also 90*b* and 91, 95 and 96, nickel steel, with 64 and 65.

§ 7. The observations upon the nickel steel when fully magnetic between 350° C. and 600° C. lie very approximately on a parabola in which the relation between the constants is such that $1/\mu . d\mu/d\theta$ has a maximum value at about 570° C., but varies so slowly with change of θ that its value is ·0041 at 500° C. and ·0042 at 650° C.—the maximum value being about ·0044. On account of the peculiarities of the meteoric iron curves a comparison cannot be obtained over this range, but the observations 92 and 93, fig. 13, correspond with a mean value of $1/\mu . d\mu/d\theta$ equal to

·0039. It is curious that for a sample of nearly pure iron, examined in the same way as the nickel-iron alloys, the mean temperature coefficient between approximately the same temperatures was found to be nearly the same as those of the alloys, viz., ·0037 (between 630° C. and 480° C., H = ·43), although the mean permeability of the iron was more than four times that of the meteoric iron and more than double that of the nickel steel.

§ 8. The data 63 to 69, &c., nickel steel, show that the reversible fully magnetic state of the material extends between the air temperature and 610° C. If the heating is continued beyond 610° C.—for example to 640° C. as in 72—irreversible effects are produced (shown by the magnetic behaviour on cooling). This is interesting as showing that the change of internal structure begins below the temperature of maximum permeability of the material as a whole. (*Cf.* Section IV., § 8, p. 63.)

The fact that the loss of magnetism is very gradual in nickel-iron alloys instead of being very sudden as in nearly pure iron is clearly in accord with the theory of the process by which the alloys lose their magnetism. In iron the temperature at which the permeability becomes practically indistinguishable from that of the air is only a few degrees above that at which $d\mu/d\theta$ first becomes negative. In each of the alloys there were about 130° C. between the corresponding temperatures. (*Cf.* Section V., § 4, p. 69.)

§ 9. If the heating is interrupted at some temperature between that at which the magnetism begins to disappear and that at which it has become inappreciable, and if the temperature is then varied between this temperature and some lower temperature above that at which the solution becomes labile (*cf.* fig. 26, III.), the changes in the amount of crystallisation can, as already explained, be represented graphically by the curve $r'r''s's''$ (figs. 26, III., and 27, IV.).

The agreement between this deduction and the permeability data is shown by the experiments r'' (163), s' (164), s'' (165); r'' (173), s' (174), s'' (175), meteoric iron, 2nd winding, fig. 15.

§ 10. The cases in which heating, interrupted at some temperature between B and C (fig. 27, IV.) is followed by uninterrupted cooling to the air temperature may next be considered (*cf.* fig. 26, II.).

The two cases which will differ most from each other are represented in fig. 27, V.

In the first (qq'), the heating is interrupted soon after solid solution has begun to form, *i.e.*, soon after magnetism has begun to decrease.

In the second (rst'), the heating is not interrupted until the magnetism has nearly disappeared.

In the former case, in accordance with the explanation already given (*cf.* fig. 26, II.), the solid solution, rich in nickel, will deposit crystals (at a decreasing rate) as the temperature falls. It will become still richer in nickel during crystallisation (*cf.* Section V., § 2, p. 67) and will itself not become labile until a low temperature is reached. Hence, over a considerable range of falling temperatures, the state of the material will differ from that of complete crystallisation represented by AB (fig. 27) only in the respect that very thin layers of solid solution will be present. All of the alloy will be magnetic, with the exception of thin intervening gaps of non-magnetic material. The permeability variation for a considerable range (below a temperature at which the rate of crystallisation has become inappreciable) will be precisely the same as when the material is in the state corresponding to the curve A*a*. At each temperature the permeability will be less in a constant proportion than when the material is wholly magnetic.

The extent to which this conclusion is verified is shown by the following data :—

NICKEL Steel (see Curves, fig. 21) Cooled from 689° C.

Number of experiment.	(75).	(76).	(77).	(78).	(79).	(82).
μ	4·53	2·90	1·80	1·39	0·85	1·39
μ_0	—	3·58	2·42	1·74	1·11	1·8
μ/μ_0	—	0·81	0·75	0·80	0·77	0·77

The values of μ_0 were obtained from the curve joining points 63 to 69 (Nickel Steel, fig. 18), by interpolation, for temperatures corresponding to (76), (77), &c.

In the second case of fig. 27, V., in which the heating is interrupted at a comparatively high temperature, the change in the degree of crystallisation will proceed in a different way. There is at first a considerable amount of solid solution comparatively weak in nickel, and the temperature is relatively high. During the early stages of the cooling there will be a considerable amount of crystallisation round the existing nuclei, and the solution round these nuclei will become comparatively rich in nickel. The main portion of the solution will, however, remain weak in nickel, and will become labile when that temperature is reached which is represented by the point of intersection of the horizontal line through *r* and the curve C′B′A (*cf.* fig. 26, II.). Subsequently crystallisation will proceed from this solution exactly as when uninterrupted cooling took place from a temperature higher than C.

But the portions of the solution from which crystallisation took place during the stage represented by *rs* will have become of similar content in nickel to the solution existing at *q* in the first case, and will not become labile until a low temperature is attained. The permeability variation, for a considerable range below a temperature such as *f* (fig. 27, V.) will be the same on cooling from *r* as on cooling from C, but the permeability itself will be less in a constant proportion at each temperature in the former case than in the latter. This will happen, in spite of the greater amount of total crystallisation represented by the curve *rst′* in comparison with the curve

C′B′A, because of the well-known effect of gaps in a magnetic circuit. The amount of crystallisation at f' is greater than at f, for example, but the excess results from crystallisation round nuclei, which is accompanied by the production of layers of non-magnetic material which surround these nuclei.

These conclusions can be tested by examination of the relation between the permeability data obtained during the cooling of the nickel steel from 810° C. and from 750° C. respectively.

The data are given in the tables (p. 46) in the experiments from 20*b* to 28 and from 50 to 58. The relation between the permeability variations in these two series of observations is shown graphically in fig. 20 (nickel steel), in which the unnumbered dotted curve corresponds with that drawn through the points 21 to 29 in fig. 18.

The quantitative relation between the data is shown in the table below :—

NICKEL Steel (see Curves, figs. 18 and 20).

Number of experiment.	(50).	(51).	(52).	(53).	(54).	(55).	(57).	(58).
μ	0·395	0·76	1·705	1·49	1·38	1·245	0·97	1·37
μ_0	—	0·1	2·45	1·96	1·80	1·63	1·255	1·80
μ/μ_0	—	7·6	0·70	0·76	0·77	0·76	0·77	0·76

The values of μ_0 were obtained, by interpolation from Experiments 21 to 29, for the temperatures corresponding to 51, 52, &c.

From these data it is seen that below 460° C. the permeability variations in the two cases are practically identical, and that the value of the permeability in the one case is about three-fourths of the corresponding value in the other (*cf.* Section IV., § 8, p. 62).

It is also seen that the observations 50, 51 (fig. 20) agree with the view that crystallisation round crystals already present takes place above 650° C. The rapid rise of permeability between 51 and 52 is consistent with the hypothesis that the bulk of the solution present at 50 began to crystallise from the labile state at about 650° C. This temperature is approximately that at which a permeability curve, corresponding to a constant amount of crystallisation and passing through 50, would cut the curve through 21 and 22 (see fig. 18).

§ 11. The explanatory value of the theory is still further confirmed by the measurements, after interrupted cooling, of the permeability at the temperature of the air.

It was noticed frequently (see Section IV., §§ 5, 7 and 8) that the permeability at the air temperature was less after interrupted cooling than when the cooling from beyond the critical point was continuous. That such effects are to be expected will be seen on consideration of fig. 27, VI. If the cooling is interrupted at a comparatively high temperature such as v_1, crystallisation will proceed from the metastable solution during subsequent reheating to w_1 and cooling to x_1. At the latter point the bulk of the solution has again reached the temperature of lability, and crystallisation proceeds by generation of fresh nuclei. But the solution from which crystals separated, during the treatment $v_1w_1x_1$, has become relatively rich in nickel and will not become labile until a temperature lower than x_1 is reached. The value of this temperature will depend upon the amount of crystallisation that ensues during the process $v_1w_1x_1$.

If it is comparatively small, the whole of the solid solution remaining at p_1 may be in the labile state, and crystallisation during further cooling will take place in the same way as when the cooling from C is uninterrupted.

If, however, there is a considerable amount of re-crystallisation during the process $v_1w_1x_1$, or if the amount is increased by repetition of the process as in the case $v_2w_2x_2y_2z_2$, then the solution from which crystals have been deposited round nuclei may have become so rich in nickel that it does not become labile until a low temperature, such as p_2, is attained. The mean permeability of the material at the air temperature may then be relatively low.

Examples of the correspondence between these conclusions and the experimental data are given below.

Meteoric Iron I. v (45), w (46), x (47).

Here the range of the alternation is about 60° C. and the permeability x is about $8\frac{1}{2}$ per cent. greater than the permeability v.

The subsequent air temperature permeability (Experiment 48) is about 4 per cent. less than that obtained after continuous cooling (*cf.* Experiment 49).

Meteoric Iron II. (Curves, fig. 11). v (26), w (27), x (28).

Here the range of the alternation is about 100° C. and the permeability x is about 16 per cent. greater than the permeability v.

The subsequent air temperature permeability (29) is about 6 per cent. less than that obtained after continuous cooling (111).

v (30), w (31), x (32), y (33), z (34).

Here, after two alternations over a range of about 100° C., the subsequent air temperature permeability (35) is about 11 per cent. less than after continuous cooling (Experiment 111).

Nickel Steel (see Curves, fig. 22). v (94), w (95), x (96).

Here, after a single alternation over about 60° C., the permeability x is about 23 per cent. greater than v, and the subsequent air temperature permeability (97) is about 16 per cent. less than that after continuous cooling (85).

It is important to notice that even in a case like $v_1w_1x_1p_1$, in which it is assumed that all the solution remaining at p_1 is simultaneously labile, just as when the cooling is uninterrupted, the permeability may be less below p_1 than after continuous cooling. For, in the former case, if the cooling has not taken place sufficiently slowly, the portions of the solution of which the crystallisation has been retarded (by the deposition from them of crystals less rich in nickel than themselves) may give rise eventually to crystals containing an appreciably greater percentage of nickel than is contained by the original nuclei which they surround.

Thus interrupted cooling may, on account of the incomplete equilibrium due to difficulty of diffusion, be followed by a less homogeneous crystallisation of the material as a whole than when the cooling is continuous. If this does occur, the permeability will be less in the less homogeneous material, because (*cf.* HOPKINSON, 'Roy. Soc. Proc.,' *loc. cit.*, p. 70, above) the permeability of a nickel-iron alloy in a given weak field decreases as the percentage of nickel increases towards 25.

§ 12. Owing to the comparative lowness of the temperatures at which the last stages of the crystallisation occur, it is probable that the greatest degree of homogeneity will not be attained unless the cooling is extremely slow and that, if the cooling is comparatively rapid (occupying only a few hours), the formation of mixed crystals will be incomplete at ordinary temperatures. A subsequent alternation of temperature between that of the air and a higher temperature (below that at which solid solution begins to re-appear) will then produce a perceptible effect upon the permeability-temperature curve. It will accelerate the passage of the material into the state of final equilibrium, to be expected theoretically, in which the crystallisation is complete and the composition of the crystals is uniform.

The experiments 97 to 107 (nickel steel, p. 47) may be cited as an example of the effects of such alternation. The data are shown graphically in fig. 22 (nickel steel). Precisely similar effects are shown also in figs. 17, 19, and 20. From each of the curves it seems that, during reheating, little effect is produced until the temperature exceeds 450° C.; but, beyond this, there is a considerable accession of permeability (*cf.* Section VII., § 11, p. 101). The effect is most noticeable in those cases in which the previous value of the permeability at the air temperature is low.

SECTION VII.—THE COMPOSITION OF THE SACRAMENTO METEORITE AS DETERMINED BY THERMOMAGNETIC ANALYSIS.

§ 1. A comparison of the thermomagnetic curves of the meteoric iron with those of the artificial alloy, and with the data given by OSMOND and others, shows, in the first place, that the iron consists largely of an alloy containing about 6 per cent. of nickel. This agrees with the result derived from chemical analysis, that the kamacite of octahedral iron contains between 6 and 7 per cent. of nickel. As already shown (see, *e.g.*, the magnified photograph of the core, Plate 1, fig. 4), the present meteorite consists mainly of kamacite.

§ 2. The thermomagnetic behaviour of the meteorite at temperatures below 500° C. shows, however, that its structure is complex, that it does not consist wholly of the $6\frac{1}{2}$ per cent. alloy, kamacite. This is seen in the curves for the first winding (fig. 9), and again very clearly in fig. 14, second winding. The latter shows, in greater detail than the former, that there is an irreversible alloy present in which magnetism disappears at about 480° C., and reappears near the temperature of the air. It is seen that this alloy behaves, on interrupted heating, in the way characteristic of irreversible alloys.

Inspection of the available experimental data shows that the alloy having the thermomagnetic properties just stated is the richest in nickel of the irreversible alloys, and contains about 27 per cent. Ni.

The results thus point to the conclusion that the thin bands of nickel-rich alloy which occur in the meteorite contain between 25 and 30 per cent. of nickel. The geometrical distribution of the taenite in the ring has already been described (Section I., § 5, p. 25) and its loss of magnetism would clearly produce gaps in the magnetic circuit and consequent diminution of permeability.

The amount of nickel-rich alloy in the material is proved to be small not only by inspection of the etched surface, but also by the chemical analyses (Section I., §§ 2, 3, pp. 23, 24) of the meteorite as a whole. If the meteorite contains m per cent. of Ni, and the kamacite and taenite k and t per cent. of Ni respectively, then the number of grammes of taenite in 100 grammes of the meteorite is

$$x = 100\,(m-k)/(t-k).$$

This assumes, of course, that the distribution of the kamacite and taenite is uniform (*cf.* the analyses by FOOTE, p. 23, and WRAIGHT, p. 24).

If we assume that in the present case, in round numbers, $m = 7{\cdot}3$, $k = 6{\cdot}5$, and $t = 27$, then $x = 4$ approximately, *i.e.*, only about 4 per cent. of the meteorite can consist of taenite.

Inspection of the curves of fig. 14 (see p. 56) shows that when the nickel-rich constituent is magnetic the permeability of the ring is over 60 per cent. greater than when it is not magnetic, but 4 per cent. of the nickel-rich constituent is quite sufficient to account for this difference. Thus, if a ring contains x per cent. of an alloy of permeability μ_2 arranged as a single transverse gap in the rest of the material (which is of permeability μ_1), the equivalent permeability of the whole ring will be

$$\mu = \mu_1\mu_2 \Big/ \left\{\mu_2 + \frac{x}{100}(\mu_1-\mu_2)\right\}.$$

If $x = 1$ and $\mu_1 = 100$, then, when $\mu_2 = 1$, the permeability will be

$$\mu = 50{\cdot}25,$$

i.e., the presence of 1 per cent. of a non-magnetic alloy would reduce the permeability to half the value it would have if the non-magnetic alloy were replaced by material of the same permeability as the rest of the ring.

If $\mu_2 = 5$, then, when $x = 1$,

$$\mu = 84 \text{ approx.},$$

i.e., the permeability in the case just considered would be increased nearly 70 per cent. if the permeability of the material in the gap rose from $\mu_2 = 1$ to $\mu_2 = 5$.

The permeability of the kamacite in the field used in the experiments is more than 100 (Section III, § 7, p. 40), and that of a 27 per cent. alloy when magnetic is at least 5 in the same field (*cf.* HOPKINSON'S curves, 'Roy. Soc. Proc.,' 1890). Hence the loss or gain of magnetism by the small quantity of the richer alloy known to be present, occurring transversely in the ring, would produce an effect of the kind and relative magnitude shown in fig. 14.

§ 3. The curves of fig. 14, in conjunction with the other data, prove that, at the end of the experiments, the meteoric iron consisted almost entirely of two irreversible alloys, viz., a small quantity of an alloy containing between 25 and 30 per cent. of nickel and a relatively large quantity of an alloy containing between 6 and 7 per cent. of nickel. After the experiments the ring was polished and etched and showed a distribution of the kamacite and taenite which, as far as careful examination through a lens could decide, was identical with that existing in the core in its original state.

Hence, although the internal structure of the taenite may have changed during the course of the experiments, its distribution with respect to the rest of the meteorite remained practically unaltered. At the end of the experiments it was an irreversible alloy containing about 27 per cent. of nickel.

But a careful examination of the data obtained at different times after the beginning of the thermal treatment seems to show conclusively that the taenite was subject to alteration of internal structure during the course of the experiments and did not, at the outset, possess the same properties as the artificial alloy containing 27 per cent. of nickel.

The evidence, as will be seen, supports the hypothesis that the taenite was originally a mixture, thermomagnetically discernible, of a nickel-poor alloy such as kamacite and of a much richer alloy containing not less than 37 per cent. of nickel.

If, as before, we assume that the taenite contains t per cent. of Ni and that it is a mixture of kamacite containing k per cent. of Ni and of an alloy containing t' per cent. (where t' is greater than t), the number of grammes of kamacite in 100 grammes of the eutectic will be

$$x = 100\,(t'-t)/(t'-k),$$

and if we assume that, in round numbers, $t' = 40$, $t = 27$ and $k = 6{\cdot}5$, then

$$x = 39 \text{ approx.},$$

or, roughly, 40 per cent. of the eutectic will consist of kamacite.

Having, for the sake of directness, stated this view at the outset, the arguments in its favour may now be given.

§ 4. A preliminary experiment was performed soon after winding of the ring to find approximately the maximum permeability of the material. It gave the following numbers :—

Temperature.	H.	μ.
° 658 (approx.)	0·20 0·31	7·91 8·23

Previously, the ring had been heated only once to a high temperature, viz. to a dull red, during a preliminary testing of the heating apparatus. The permeabilities are given in the same arbitrary units as those of the figure for the first winding (see Section III., § 6, p. 39).

After the above measurements the ring was heated twice to a temperature above 800° C. Some months later the permeability was again measured, at temperatures comparable with the above, with the following results :—

Temperature.	H.	μ.
° 622	0·43	4·72
661	0·445	5·17
678	0·44	4·38

Making every allowance for possible error of experiment and for the isolated character of the experiments first cited, it would seem to be proved that heating above 800° C., in the early stages of the heat treatment, is followed by a considerable lowering of the maximum permeability.

This conclusion is supported by the numbers given in the previous tables (pp. 42 to 45). The maximum permeability seems to have become gradually smaller as the experiments proceeded. Thus, whereas the maximum permeability first quoted above corresponds approximately to $\mu = 1000$ C.G.S., the highest value observed towards the end of the experiments during the first winding did not exceed 700 C.G.S. (H = 0·48). The data obtained during the second winding show that at the end of the experiments the maximum permeability of the ring probably did not exceed 600 C.G.S. (H = 0·43).

Although part of the decrease may have been due to oxidation of the ring, the results are clearly in accord with the hypothesis of a conversion of the nickel-rich and nickel-poor constituents of the taenite into a mixture which becomes non-magnetic at a temperature below that at which the permeability of one of the original constituents is a maximum. Similarly, if the maximum permeability observed during cooling is compared with the value observed at the corresponding temperature during heating it will be seen that it is relatively less in the second winding than in the first. Thus in the one case the ratio (at 540° C.) is about 1 : 2 and, in the other about 3 : 5. It is possible that part of this difference is due to the more gradual cooling in the first experiments; but part of it is possibly also due to decrease in the total amount of the nickel-poor alloy.

§ 5. If the values of permeability obtained below 500° C. during the 1st winding (when the meteorite had been heated only a few times to a high temperature) are compared with those of fig. 14 (representing the behaviour of the material after a large number of heatings), it will be seen that there are notable differences.

The field strengths (·48 and ·43 respectively) are different in the two cases; but the data already referred to show that the permeability variation with the field strength is not rapid enough to make this difference very important (*cf.* Section IV., § 2, p. 41). It is seen from the curves, however, that the percentage differences between the greater permeabilities at temperatures below 400° C. and those obtained at corresponding temperatures after continuous cooling from 800° C. are much less in the earlier than in the later experiments. The maximum value at the air temperature (assuming that the calculated constants of the two windings are substantially correct) is about the same at the end as at the beginning of the experiments, viz., about 280 and 270 respectively. But, in accordance with the statement above, the permeability at the air temperature after continuous cooling from 800° C. (about 220 C.G.S.) is considerably greater in the earlier than in the later experiments (about 170 C.G.S.).

These results agree with the interpretation (see below) that, after continuous cooling from 800° C., the gaps in the magnetic circuit at 15° C. (due to the taenite) are less at first when the taenite contains an appreciable amount of nickel-poor alloy and of nickel-rich alloy, separately magnetic at that temperature, than later, when practically the whole of the taenite may be non-magnetic.

§ 6. Upon heating from 15° C. the permeability decreases continuously in the earlier experiments until a temperature of about 300° C. is reached—the decrease being especially marked in the curves of greatest permeability (see fig. 9, 1st winding)—while in the later experiments the decrease is scarcely perceptible in the lowest curve and ceases below 100° C. in the curve of greatest permeability (see fig. 14, 2nd winding).

Thus in the first case the maximum decrease between 15° C. and 160° C. is about 12 per cent. and the minimum about 5 per cent.; in the second the maximum decrease (between 15° C. and 90° C.) is about 2·5 per cent. and the minimum is less than 0·5 per cent.

This decrease of permeability is of importance, whatever its interpretation may be, since it is peculiar to the meteoric iron. No similar phenomenon is shown, to my knowledge, in any of the permeability curves of nickel-iron alloys for weak fields published hitherto; but there is no doubt of its existence here since, as will be seen from the data, it was observed repeatedly.

Now, just as the data already cited indicate that the taenite contains a nickel-poor constituent which disappears or becomes magnetically undetectable under thermal treatment, so those just mentioned point to the presence of a nickel-rich constituent which behaves in the same way.

§ 7. By inspection of the curves drawn from OSMOND's data (with which the less complete results published by HOPKINSON and by DUMONT are in accord) it will be seen that an alloy containing more than 30 per cent. of nickel loses during heating, and regains during cooling, the greater part of its magnetic properties at a temperature above 15° C., which is higher in proportion as the nickel content (below 70 per cent.) is greater. When the magnetic change (now approximately reversible) takes place at 300° C., the alloy contains about 37 per cent. of nickel (DUMONT, 'Comptes Rendus,' vol. 126, p. 742, 1898, gives 300° C. as the temperature of disappearance in a particular alloy containing 39·4 per cent. Ni).

Suppose that the taenite is originally a *comparatively* coarse mixture of alloys containing approximately 40 and 6 per cent. of nickel which exist together in such proportions that the taenite as a whole contains roughly 27 per cent. of nickel. The effect upon such a mixture of repeated heating to a high temperature and cooling under ordinary conditions will be to produce eventually the artificial alloy containing 27 per cent. of nickel in which the structure is comparatively fine (see below, Section VIII., § 2, p. 104, and § 11, p. 108).

During the first heating of the meteorite, after the original crystallisation, the permeability of the 6 per cent. alloy in the taenite will rise continuously to 650° C. That of the 40 per cent. alloy will rise at first, but will subsequently reach a maximum and afterwards practically disappear at about 350° C. (This was not observed—the material having been heated to dull redness, as already explained, before any observations were taken.) Above 750° C. the taenite will consist of two non-magnetic substances containing different percentages of nickel. During the first heating to 800° C. and the subsequent cooling there would be appreciable interdiffusion of these constituents.

In subsequent heatings (the material being raised to a high temperature between each) there would, on this hypothesis, be 6 per cent. and 40 per cent. alloys and also all intermediate artificial alloys in varying proportions. Gradually, however, the material as a whole would approach the condition of the artificial alloy of the same composition. Comparatively few heatings would be sufficient to convert the more intimately mixed portions of the 6 per cent. and 40 per cent. alloys into the artificial 27 per cent. alloy.

The early evidence of the presence of this alloy (shown in fig. 9) proves that much of the mixture is intimate.

When all the taenite had been converted into the artificial 27 per cent. alloy, the behaviour of the material as a whole would be as follows:—The permeability would rise continuously during heating at first, would reach a maximum in the neighbourhood of 400° C., would then fall comparatively rapidly until the rate of increase of permeability due to increase in temperature of the 6 per cent. alloy (of which the meteorite is mainly composed) over-balanced the rate of loss due to increase in temperature of the 27 per cent. alloy. The magnetism of the latter would finally disappear at about 490° C., and, if the heating were then discontinued, the permeability would remain lower than at the corresponding temperature during heating until, towards the temperature of the air, the permeability would become subject to a comparatively rapid increase.

§ 8. Inspection of fig. 14 (2nd winding) shows that this is almost exactly what is observed after the material has been heated a large number of times. The only essential difference is that there is still at first a small decrease in permeability, which ceases below 100° C., and which would be accounted for if there were still in the taenite small quantities of alloys containing slightly more than 27 per cent. of nickel.

On the other hand, when the material has been heated only a few times, the variation is different, as shown in the curves for the 1st winding. Here there is a pronounced decrease of permeability between 400° C. and 450° C. as before—pointing to the presence of a considerable amount of 27 per cent. alloy; but there is also another pronounced decrease during the first stages of the heating from 15° C. This is obviously what would occur if, besides the artificial 27 per cent. alloy, there were still appreciable quantities of alloys containing amounts of nickel intermediate between 27 and 40 per cent.

In the lower curve (*cf.* Experiments, *a*, *b*, *c*, Section IV., § 3, p. 42) the decrease continues approximately to 300° C., and hence in these early observations there is detectable the alloy containing at least 37 per cent. of nickel (see fig. 23).

§ 9. Of special significance is the peculiarity, above referred to, of these earlier and of the later curves, namely, that the percentage decrease of permeability at lower temperatures during heating is much greater when the permeability follows the upper curve than when it follows the lower.

This peculiarity will be seen by comparison of the experiments *a* and *b*, 33 and 34, 1st winding, with the experiments 1 and 2, 39 and 40, and also of the experiments 111 and 112, 2nd winding, with 119 and 122.

These results are in complete accord with the interpretation of the magnetic phenomena which is advocated. In the lower curves the permeability is relatively small, because (see § 11, below, p. 100) most of the irreversible 27 per cent. alloy has not undergone the transformation into the magnetic state. There are, in consequence, gaps in the magnetic circuit at 15° C. which are absent when the 27 per cent. alloy is magnetic—as it is when the upper curve is obtained. Consequently, during heating in the first case, the loss of magnetism by the reversible alloys merely causes increase of size in gaps already present, while in the second case the gaps are absent initially and are produced by the loss of magnetism of these reversible alloys.

Now the effect upon the induction through a circuit of the formation of a small transverse gap is very much greater when no gap is present initially than when the gap formed merely increases the size of one already in existence. Thus the induction B (in a given field), when there is a transverse gap equal to the fraction θ of the circumference in a ring of permeability μ, is

$$B = B_0/\{1+\theta(\mu-1)\},$$

where B_0 is the induction when the gap is absent. And since, from the above expression,

$$dB/d\theta = -B(\mu-1)/\{1+\theta(\mu-1)\},$$

it is seen that the effect of a small increase, $d\theta$, in the gap is greatest when $\theta = 0$, and, assuming $\mu-1 = 100$ (which is approximately the case in the present experiments), the percentage variation of B with θ is twice as great when $\theta = 0$ as when $\theta = 1/100$.

The above expressions apply only when the permeability of the material which loses its magnetism is assumed to be the same as that of the rest of the material. If the permeability of the former is less than that of the latter, the effect is of the same character, but less pronounced in proportion as the difference between the permeabilities increases; but the above computation is sufficiently accurate for the present purpose. It shows, when compared with the numerical data in the tables, that the effects observed are of the order of magnitude theoretically deducible, and confirms the view that they are due to the formation of breaks in the magnetic circuit in the way described.

§ 10. The thermo-magnetic data seem thus to point to the correctness of the view that the taenite is composite, that it is transformed by successive heatings into a relatively more homogeneous alloy (containing between 25 to 30 per cent. of Ni) and that the transformation takes place by the gradual interdiffusion of its richer and weaker constituents (containing probably not less than 6 per cent. of Ni in the one case and probably not more than 40 per cent. of Ni in the other).

Fig. 28 summarises the evidences for these conclusions. The full curves indicate the condition of the meteoric iron after it had been heated four times above 800° C. They have been plotted from the numbers given in the table on pp. 42, 43, using the constants of the 1st winding given on p. 39. The dotted curves indicate the state of the material after it had been heated about twenty times above 800° C., including once above 900° C. They were plotted from the data on pp. 43 to 45, using the constants

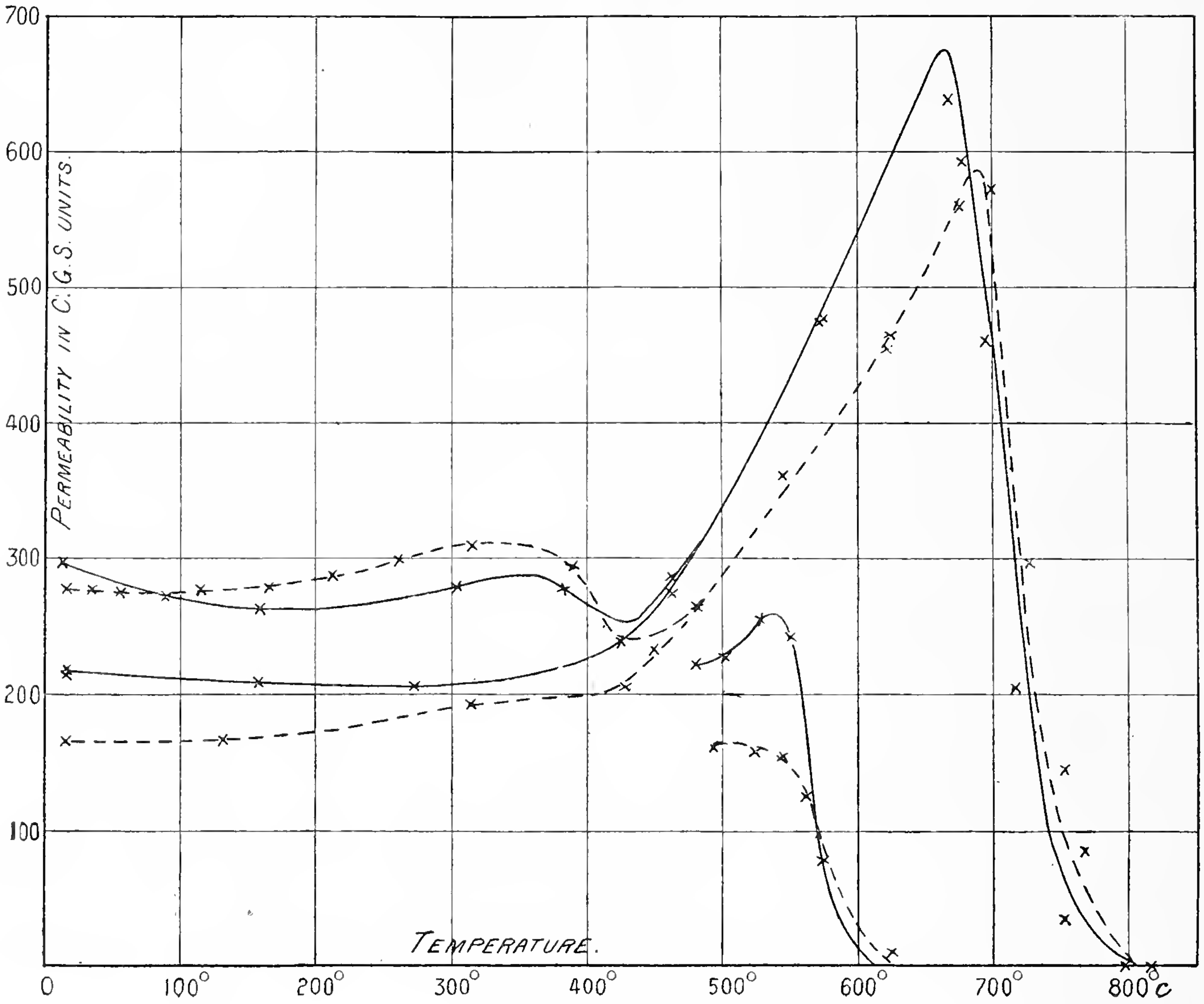


Fig. 28. Meteoric iron.

Permeability changes produced by repeated heating.

of the 2nd winding stated on p. 39. The greater distance of the lower dotted curve below the lower full curve at the air temperature than at temperatures above 350° C.; the greater permeability at temperatures above 100° C. on the upper dotted curve than on the upper full curve, and the greater permeability above 500° C. on the full curve than on the dotted curve, are all in accord with the interpretation given of the gradual change of the taenite produced by repeated heating.

§ 11. There is only one further point with respect to the curves for the meteoric iron that remains to be discussed, viz., the cause of the fact that the 27 per cent. irreversible alloy does not become magnetic at the normal temperature, for such an alloy, during the first cooling from 800° C.

It is probable (Section VI., § 5, p. 86) that an irreversible alloy containing only 6 per cent. of Ni is not completely transformed into the magnetic state during cooling until its temperature is near that of the air. The transformation is accompanied by considerable increase in volume. Hence, since the later stages take place at a low temperature, when the rigidity of the material is comparatively great, a considerable amount of internal strain may arise. It is in the already strained material that the transformation of the 27 per cent. alloy has to begin.

But if the material is subsequently heated to a temperature not high enough to cause the 6 per cent. alloy to begin to undergo the magnetic transformation in the reverse direction, the internal strain in this alloy will be diminished. The effect of such heating will be to make more homogeneous the distribution of iron and nickel throughout the material (Section VI., § 12, p. 92). A sufficient number of heatings would convert it from a heterogeneous mixture of alloys containing different percentages of Ni losing and gaining their magnetic properties at different temperatures into a homogeneous alloy magnetic at all temperatures between 15° C. and 600° C.

When the temperature is reached, during cooling, at which the 27 per cent. alloy (imbedded in the now more homogeneous alloy) tends normally to become magnetic, its transformation—retarded at first, perhaps in a way analogous to the depression of the freezing-point of water by pressure—may become possible. Indeed, when it is remembered (*cf.* HOPKINSON and GUILLAUME) that an irreversible alloy rich in nickel increases by about 2 per cent. in volume as it changes from the non-magnetic to the magnetic condition, it is clear that an appreciable part, at least, of the observed retardation must be due to an effect of the kind just mentioned.

§ 12. The views expressed in the above and in the preceding paragraphs were confirmed by some experiments on the effect of thermal treatment upon the density of the meteoric iron, in which it was found that changes in density corresponding with the changes of permeability produced by heating to different temperatures, as above described, could be observed; but these experiments are omitted for the present from considerations of space.

It may be mentioned, however, as showing the advantages of the thermomagnetic method of analysis, that a change in the taenite which produces an alteration of over 50 per cent. in the permeability of the meteorite is not enough to produce a change of more than 0·1 per cent. in the density.

§ 13. If the conclusions already given are correct, it is possible to discuss with some confidence the conditions under which the characteristic structure of meteoric (octahedral) iron has arisen.

Suppose that the alloy is comparatively poor in nickel, *i.e.*, that it contains only a little more than the minimum amount necessary for the existence of Widmanstätten figures, and suppose further that the structure is acquired during cooling of the alloy from a comparatively high temperature.

The material will be a homogeneous solid solution of iron and nickel at temperatures above 700° C. Below this temperature the solution is metastable, but spontaneous crystallisation (see Section VI., § 1, p. 78) cannot occur until a temperature of about 600° C. is reached. The solution then becomes labile, and spontaneous generation of nuclei can take place. If the subsequent rate of cooling is extremely slow the crystallisation will proceed (see p. 79) around the first nuclei.

Suppose that these original nuclei are arranged in the form of an octahedral network (*cf.*, *e.g.*, the crystals of steel described by TSCHERNOFF, 'Metallographist,' vol. 2, 1899, p. 74) and that the material is of comparatively uniform composition, so that the octahedral lamellæ of crystalline nuclei are at nearly uniform distances apart. These nuclei will contain a relatively small percentage of nickel (see Section V., § 2, p. 67, also fig. 23), and the remaining solid solution will contain a greater percentage of Ni than the meteorite as a whole. If the cooling continues extremely slowly, crystallisation will proceed around the nuclei from the metastable solid solution. The crystals (both the nuclei and the deposits around them), and also the solid solution, will gradually get richer in nickel (*cf.* Section VI., § 3, p. 85).

If the rate of cooling is sufficiently slow, the strength of the solid solution (in the spaces between the octahedrally arranged bands forming round the first growth of nuclei) may continue to increase, so that its temperature remains always above that at which it passes into the labile condition. Under these circumstances there will be no further spontaneous generation of nuclei (above the eutectic temperature) after that which occurs at 600° C.

The "crystallisation" (*i.e.*, regular structural re-arrangement of the material) will proceed outwards from each of the octahedral planes along which the spontaneous re-arrangement began. The layers of solid solution (material not yet structurally re-arranged) will become gradually narrower. At the same time the layers of "crystallised" material will become wider. Throughout the whole process there will be a continual re-adjustment of the percentages of iron and nickel in the crystals and in the solid solution.

The final state of the material below the air temperature will be such that it contains layers of homogeneous nickel-poor alloy and thin intervening layers of eutectic. The actual width of each layer of nickel-poor alloy will depend upon the distance apart of the first lamellæ formed when the material reached the temperature of lability; but the ratio of the widths of the nickel-rich and nickel-poor layers (taenite and kamacite) will be nearly constant if the original distribution of lamellæ is symmetrical.

§ 14. A perceptible change in the process of crystallisation will occur if the rate of fall of temperature is more rapid than that above contemplated, so that, after the first deposition of nuclei during cooling, the solid solution does not always remain above its temperature of lability. Then the growth of crystals may be insensible between the time of deposition of one set of nuclei and the next. At each deposition crystals slightly richer in nickel than those last deposited will be formed, and a solution richer in nickel will be left. The latter will remain metastable while the temperature falls a little; then it will become labile and there will be a fresh deposition of nuclei. The crystallisation will thus proceed by spontaneous generation of successive sets of nuclei from a solid solution which gets continuously richer in nickel as the temperature falls. The strongest solution will contain about 27 per cent. of nickel, and, becoming labile at about the air temperature, will begin to crystallise then as a mixture of nickel-rich and nickel-poor alloys. At any temperature above this there will be always some solid solution, which, after partial crystallisation in the condition of lability, leaves a stronger solution which is metastable until the temperature falls.

During cooling the solid solution will never become so rich in nickel that it contains more than 27 per cent., for any solid solution containing less than this percentage can begin to crystallise by becoming labile before the eutectic temperature (about 0° C.) is reached, and when the latter temperature is attained the solid solution remaining will crystallise as a mixture of the nickel-rich and nickel-poor alloys.

In its final state the material will be roughly homogeneous, for practically the same process of crystallisation will have occurred in every small element of the mass. There will be mixed crystals containing every proportion of nickel from 2 or 3 per cent. to about 6·5 per cent. (as well as the richer crystals of the second type formed at the eutectic temperature), for the cooling will have proceeded so rapidly that the continual redistribution of nickel necessary to produce uniformity in composition of the mixed crystals (of the nickel-poor type) will not have had time to occur.

§ 15. On such a view of the process of crystallisation during cooling as is above indicated, it will be seen that a structure identical in form with that observed in the Widmanstätten figures and similar in composition to that shown by the magnetic properties is explicable. The fact that the breadth of the layers of kamacite sometimes varies from one part of a meteorite to another would be explained by difference in the rate of cooling, or in the manner of deposition of nuclei in different parts of the material. The fact that the average thickness of the kamacite bands decreases as the total percentage of nickel in the material increases can be explained in the same way. Thus, for example, in a meteorite containing a relatively high percentage of nickel, *e.g.*, 12 per cent., the whole material will exist "uncrystallised" until a temperature in the neighbourhood of 300° C. is reached. When this temperature—the temperature of lability of the metastable solid solution—is attained, crystallisation will begin; but the rate of growth round the original nuclei will be so slow (on account of the lowness of temperature) that, unless the rate of cooling is excessively slow, there will be a succession of returns to the state of lability during cooling. If we assume that the successive growths of nuclei take place in parallel octahedral layers, the final result, after the eutectic temperature is passed, will be comparatively narrow bands of kamacite with intervening thin bands of taenite.

When the percentage of nickel is higher than 15 or 20 per cent., the temperature at which the crystallisation begins will be so low that, as in the case of comparatively rapid cooling considered above, the crystallised material may appear to be homogeneous (*cf.* Section V., §§ 8 and 9, p. 71).

§ 16. It seems clear that if meteoric iron were kept for an indefinite period at a high temperature (below its melting-point), the structure which distinguishes it from artificial nickel iron, of the same percentage composition, at the air temperature should disappear. For the material should thereby be converted into a uniform solid solution which, on cooling, under ordinary conditions would undergo the same changes as take place in the artificial alloys. The disappearance of the meteoric structure would take place by interdiffusion between the taenite and the kamacite by which the original taenite layers would become eventually much poorer in nickel and the kamacite layers a little richer. This process would apparently be very slow, however, unless the temperature were raised much above the highest used in the present experiments in which very little interdiffusion of these two constituents seems to have occurred. I have attempted to show, however, from the thermomagnetic curves, that the temperature conditions permitted an analogous process, on a very minute scale, to take place within the taenite itself in the time over which the experiments extended. The taenite, initially a relatively coarse mixture in which, owing to the slowness and uniformity of the original cooling, comparatively large crystals of the two components of the eutectic were present, became gradually converted into a fine-grained mixture of the same constituents possessing appreciably different thermomagnetic properties.

SECTION VIII.—FURTHER DATA FROM ARTIFICIAL ALLOYS.

§ 1. In the preceding section an attempt has been made to establish quantitatively, from thermomagnetic data, the truth of the hypothesis, due originally to ROOZEBOOM, that nickel-iron alloys are examples of a system giving rise to a series of mixed crystals of two types and possessing a eutectic, or transition point.

The evidence is based mainly upon a study of meteoric nickel iron and, if the conclusions are correctly drawn, it follows that :—

(*a*) If the cooling alloy contains less than about 27 per cent. of nickel, the crystals which form first are of the nickel-poor type and contain, when stable equilibrium is reached, not more than 7 per cent. of nickel.

(*b*) If the cooling alloy contains more than 27 per cent. of nickel, the crystals which first form are of the nickel-rich type and contain not less than 37 per cent. of nickel.

(*c*) If the cooling alloy contains (approximately) 27 per cent. of nickel, there are formed simultaneously mixed crystals of two types, one containing not more than 7 per cent. and the other not less than 37 per cent. Ni. The transition begins (*cf.* Section VII., § 11) in this alloy at about the ordinary temperature of the air. The beginning of the transition in any other alloy occurs at a higher temperature.

§ 2. Although the existence of the eutectic is to be expected below 0° C. in any alloy containing more than 7 per cent. or less than 37 per cent. of nickel, it has not yet been identified micrographically in artificial alloys.

I have attempted to show, however, that it can be identified in meteoric iron in which the rate of cooling has probably been slow and uniform, and which has probably remained for a very long time at or below the eutectic temperature. In such alloys the segregation of the two constituents of the eutectic has proceeded to an extent that is magnetically discernible.

If the above conclusions are correct it would seem that the eutectic cannot be definitely detected microscopically in artificial alloys only because of the absence of sufficient segregation, but it is still possible that the thermomagnetic method (of which the advantages have been pointed out) may reveal its presence.

§ 3. The thermomagnetic data, for various artificial alloys, have already been discussed, but there is a further series of experiments to which reference should be made (*cf.* HONDA and SHIMIZU, 'Phil. Mag.,' 1905, pp. 548 and 642). Messrs. HONDA and SHIMIZU have not, to my knowledge, given any interpretation of their results, but they have determined the thermomagnetic properties for temperatures between about −186° C. and 800° C., and fields up to about 400 C.G.S. units, in the case of eleven nickel-iron alloys.

For the present purpose the most important data are those for a 36 per cent. alloy, and for a set of six alloys containing percentages of nickel ranging from 29·24 to 24·04. Unfortunately there are no similar data for alloys containing lower percentages of nickel.

According to the views stated above, the 36 per cent. alloy will give rise on cooling to mixed crystals almost wholly of the nickel-rich type.

Of the others, the $29\frac{1}{4}$ per cent. alloy, containing a little more than the eutectic percentage of nickel, will give first mixed crystals of the nickel-rich type, but, subsequently, when the eutectic temperature is reached, a eutectic mixture of nickel-rich and nickel-poor crystals. The 24 per cent. alloy, on the other hand, containing a little less than the eutectic percentage of nickel, will give first mixed crystals of the nickel-poor type, and, subsequently, at a lower temperature, the eutectic mixture.

§ 4. In seeking for the interpretation of the results obtained, it is necessary to consider the extent to which nickel-rich and nickel-poor crystals are likely to be thermomagnetically distinguishable.

A study of the permeability curves for nickel-iron alloys, at the air temperature after cooling from a high temperature, shows that these alloys can be divided magnetically into two classes.

When the percentage of nickel is 35 or more the alloy is magnetically soft. The "second stage" in the magnetisation curve is soon attained and the maximum permeability occurs when the field intensity reaches 2 or 3 C.G.S. units.

When the percentage of nickel is 25, or less, the alloy is magnetically hard. The hardness decreases as the nickel content is reduced. When the percentage of Ni is 25 the maximum permeability is not attained until H = about 50 C.G.S units, but even when the percentage is as low as 5, a field intensity of, roughly, 10 C.G.S. is required.

It is clear, therefore, that mixed crystals containing about 7 per cent. Ni and forming at or near the temperature of the air must, although their exact properties are not deducible *a priori*, be distinguishable magnetically from mixed crystals containing not less than 37 per cent. of nickel.

Further, the effects of temperature change upon the BH curves will be very different in the two cases.

In the nickel-rich crystals, on account of their magnetic softness, increase of temperature (below the critical temperature) will not be accompanied by increase of induction (for a given field) unless the field intensity is small. In the nickel-poor crystals, however,

$$(d\text{B}/d\theta),\ \text{H constant},$$

will not become negative until H is relatively large.

Thus, while in each case the $\mu\theta$ curve will be convex to the axis of temperature when the field is very small, it will become concave to the axis of temperature in the nickel-rich alloy under a field for which the $\mu\theta$ curve of the nickel-poor alloy is still convex.

These relations are shown in HOPKINSON'S curves ('Roy. Soc. Proc.,' 1890; *cf.* also WILLS, 'Phil. Mag.,' 1900).

§ 5. The significance of the results obtained by HONDA and SHIMIZU may now be briefly considered.

In the 36 per cent. alloy, for a field of 50 C.G.S., the permeability decreases continuously from the temperature of liquid air to that at which magnetism practically disappears (about 250° C.). The decrease is most rapid at the end, nearly half of the original magnetisability being lost between 150° C. and 200° C.

Further, there is very little thermal hysteresis during cooling and, in sharp contrast with the behaviour of the alloys containing less than 30 per cent. of Ni, the magnetic properties at 15° C. are practically unchanged by cooling to −186° C. This is clearly in agreement with the theory already given when it is remembered that 36 per cent. is approximately the nickel content of the least concentrated of the nickel-rich mixed crystals.

§ 6. In the alloys containing between 30 and 28 per cent. Ni the permeability decreases as the temperature rises from −186° C. until a temperature of about 150° C. is reached. Beyond this the permeability rises for H = 50, and diminishes slowly for H = 400, to a temperature of about 300° C. After this the permeability falls at first gradually and then very rapidly in both fields as the temperature approaches 500° C.

These data are clearly explicable if we assume that, at −186° C., each alloy is a mixture of the magnetically soft 36 per cent. nickel-iron and of a magnetically harder alloy for which the permeability increases with rise of temperature, even when H = 50, and disappears at a higher temperature than that of the soft alloy.

The character of the magnetism which first appears during cooling is significant.

If the IH curves be plotted from the data given, it will be seen that the initial small amount of magnetism at the temperature of the air is that of a magnetically soft material, and that each of the curves closely resembles that, at the same temperature, of the 36 per cent. alloy already referred to.

Further, as the temperature is reduced below 0° C., the magnetisability gradually increases; but at the same time the IH curve becomes more and more clearly that of a mixture of magnetically hard and magnetically soft materials.

§ 7. In the alloy containing 26·7 per cent. Ni the relative amount of the magnetically hard material, at −186° C., has so far increased that the initial fall of permeability during heating has practically disappeared.

The decrease of permeability of the soft material during rise of temperature is almost exactly counterbalanced by the corresponding increase of that of the hard material.

Thus over a considerable range of temperature we have a material of practically constant magnetic properties. We have, in fact, a magnetic analogue of the alloy of practically negligible thermal coefficient discovered by GUILLAUME.

The 26·7 per cent. Ni alloy is a *magnetic invar*. Its BH curves are nearly identical for values of H between 25 and 400 over a temperature range of more than 300° C. (from −186° C. to at least +120° C.).

§ 8. In the 24·4 and 24·04 per cent. Ni alloys the permeability increases as the temperature rises from −186° C., even in the strongest fields. A study of the data shows that the effect of a magnetically hard material now preponderates. The presence of the nickel-poor material is shown clearly, in the curves for the 24 per cent. alloy, by the marked increase of permeability (for H = 50) beyond 200° C., *i.e.*, after the opposing influence of the nickel-rich material has disappeared.

If the IH curves be plotted from the data given, it will be seen that the initial small amount of magnetism at the temperature of the air shown by the alloys containing less than 27 per cent. of nickel is that of a magnetically hard material and that, as the temperature falls, the hardness no longer increases rapidly with increase in the amount of magnetic material.

§ 9. All the data above, together with others from the same paper which might be cited, admit of simple interpretation if it be assumed that alloys containing between 24 and 30 per cent. of nickel consist mainly of a mixture of two materials, one nickel-rich and the other nickel-poor, forming a eutectic, and that the richer alloys contain a small excess of the nickel-rich material, whilst the poorer alloys contain a small excess of the nickel-poor material.

From these data it appears that the artificial eutectic mixture is one in which the thermal variation of permeability is relatively small over a considerable range.

A further important conclusion with respect to this eutectic is revealed by the behaviour after interrupted heating (*cf.* Section VI. above) of the 24·4 per cent. alloy as described by HONDA and SHIMIZU.

If there were no thermal hysteresis, the eutectic, which appears at about 0° C. during cooling, should disappear at the same temperature during heating. That it does not do so seems due to thermal hysteresis in the nickel-poor constituent. The nickel-rich constituent apparently loses its magnetism, without appreciable hysteresis, at about the temperature corresponding to the percentage of Ni which it contains (*i.e.*, between 250° C. and 300° C.), but that of the nickel-poor constituent persists and does not disappear until about 500° C. Hence at 400° C. the nickel-rich crystals have become converted into a non-magnetic solid solution, but the nickel-poor crystals still remain.

If the heating is continued until the solution of the nickel-poor crystals has begun, but interrupted before it is complete, there will be a partial re-growth of these crystals as the temperature falls. At the air temperature, however, a considerable portion of the nickel-poor alloy will be still in the non-crystalline (non-magnetic) condition (*cf.* Section VI., § 10, p. 88).

But below 300° C. during cooling the nickel-rich component of the eutectic (which, on account of insufficient heating, has not become incorporated with the nickel-poor crystals to form a homogeneous solid solution) will begin to regain its magnetism. Its permeability will increase rapidly as the temperature falls (*cf.* the curves for the 36 per cent. alloy).

At the air temperature the permeability of the material as a whole will be less than before heating began, because some of the nickel-poor alloy is still non-magnetic, but the material will be magnetically softer, because it now contains a relatively greater proportion of nickel-rich alloy. For this last reason also, during subsequent rise of temperature, the permeability will decrease much more rapidly than during the first heating.

Each of these conclusions is in accord with experimental data (*cf.* HONDA and SHIMIZU, *loc. cit.*, pp. 657, 658, and fig. 7, *j*, Plate XII.).

§ 10. A study of the thermomagnetic properties of alloys containing lower percentages of nickel than 24 and higher percentages than 29 will reveal more, and may show that the percentages of nickel to be ascribed to the two constituents of the eutectic are not quite as I have stated them. Meanwhile the evidence already obtained, and indicated above, seems sufficient to establish the coexistence of two constituents (in different proportions) in alloys containing between 24 and 30 per cent. Ni. The general accuracy of the interpretation given seems also assured.

§ 11. In the preceding Section VII., discussing the $\mu\theta$ curves for a meteoric iron under the influence of weak fields, I have attempted to show that the taenite consists originally of (in round numbers) 6 per cent. and 40 per cent. nickel-iron alloys intimately mixed, but sufficiently segregated to be distinguishable thermomagnetically. I have interpreted the curves on the assumption that a succession of heatings to a temperature of about 800° C. converts the material into a more intimate, *i.e.*, finer-grained, mixture possessing the properties of the artificial 27 per cent. alloy. The initial decrease of permeability, observed after treatment described in the paper, between 15° C. and 300° C., has been explained by assuming that it is due to the presence of alloys containing between 40 per cent. and 27 per cent. of nickel in a relatively coarse mixture while the destruction of "meteoric" segregation in the eutectic is still incomplete. I have since confirmed this interpretation by observing the permeability change (under the same field H = ·43 C.G.S.) during heating to 100° C. of a ring, not previously heated, cut from the core already described.

In this case there is no initial decrease, but an increase of about 5 per cent. between 15° C. and 100° C.—as would be expected if the material contained only 6 per cent. and 40 per cent. alloys.

It may be mentioned further that the micro-photographs of taenite given in fig. (5*d*), Plate 2, closely resemble those of well-known examples of "sorbitic," or finely-segregated, pearlite (*cf.* Osmond, 'Microscopic Analysis of Metals,' pp. 88 and 89, 1904). The two fragments of taenite (seen in fig. 5*d*) appear to belong to differently orientated plates; but such structural details as are shown in the original negative are difficult to reproduce, and no quantitative value is claimed for the figure. Better photographs could probably be obtained after a more prolonged search than was made while the apparatus was at my disposal; but even the best microphotographs of fine-grained structures frequently leave room for doubt with respect to their significance. On the other hand, if two constituents of a material have thermomagnetic properties which are sufficiently distinct, their coexistence will be demonstrable without doubt by the magnetic method, however fine grained the microstructure may be.

§ 12. In conclusion, it seems reasonable to hope that the theory advocated will prove to be an adequate basis of correlation of the properties of all alloys of nickel and iron, and that the thermo-magnetic method is capable of further development as a means of observing continuously and of interpreting changes in the internal structure of magnetic alloys.

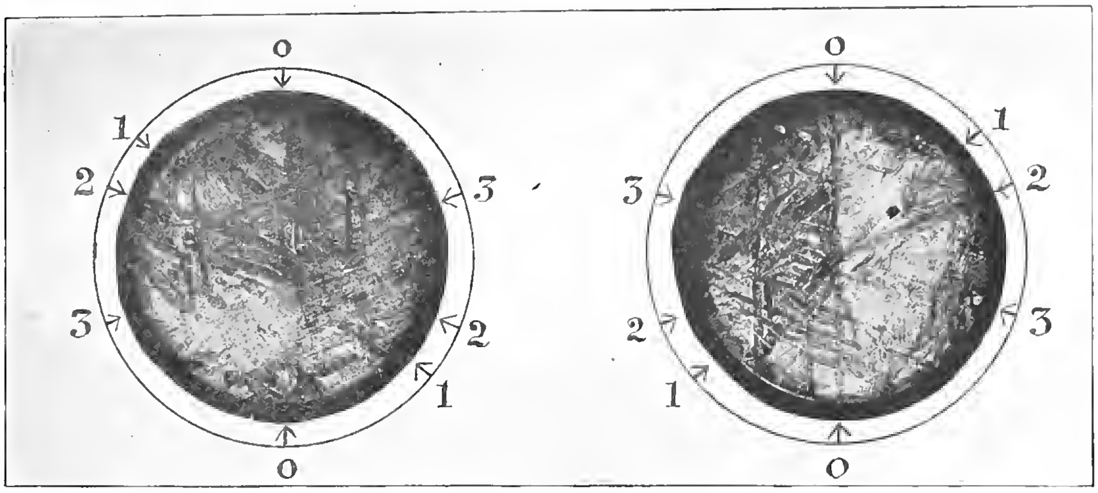


Fig. 2.

Fig. 3.

(Natural size.)

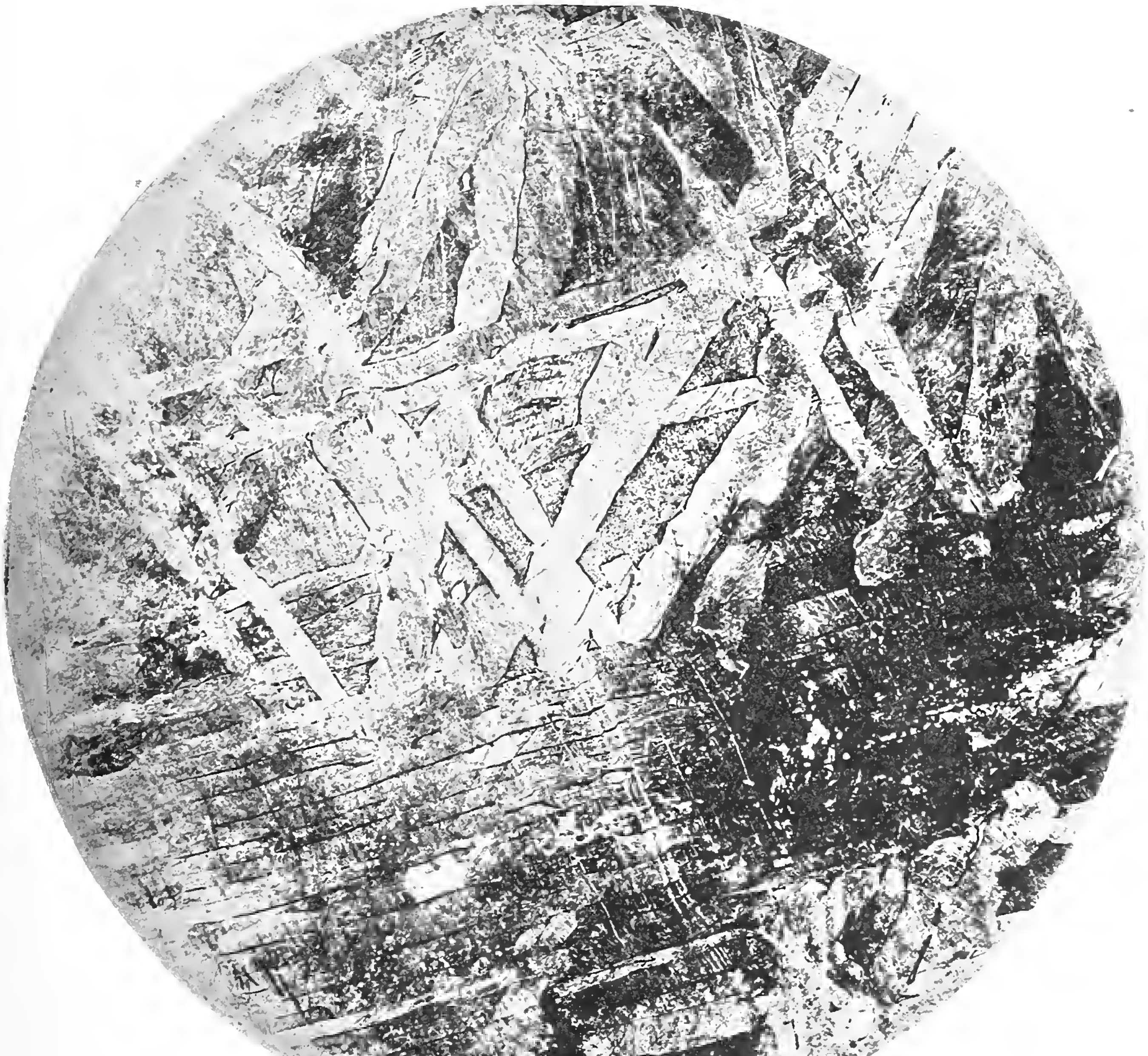


Fig. 4.

(Enlargement of the negative of fig. 2.)

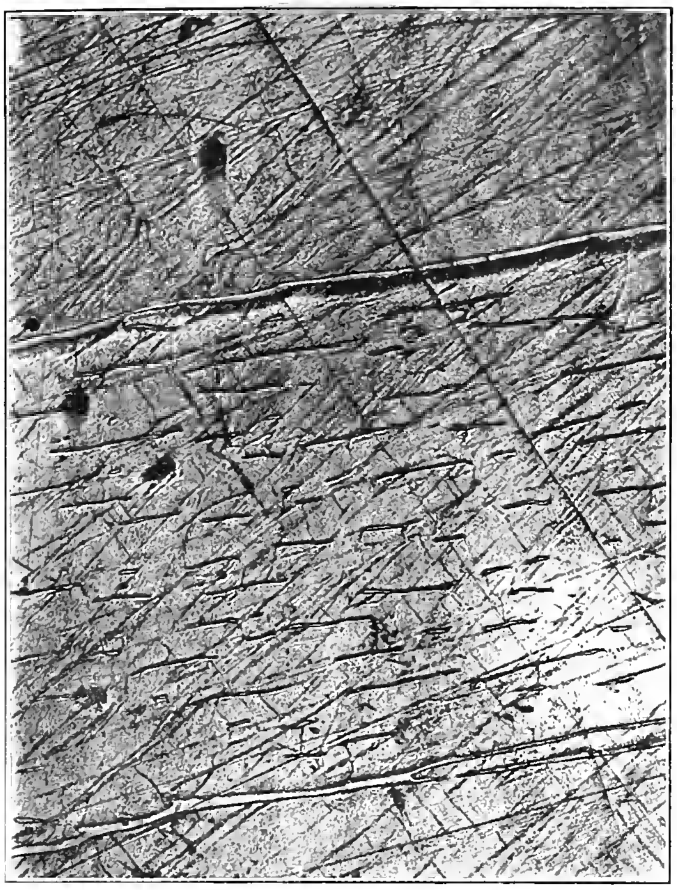


Fig. 5*a*.
× 50 diameters.

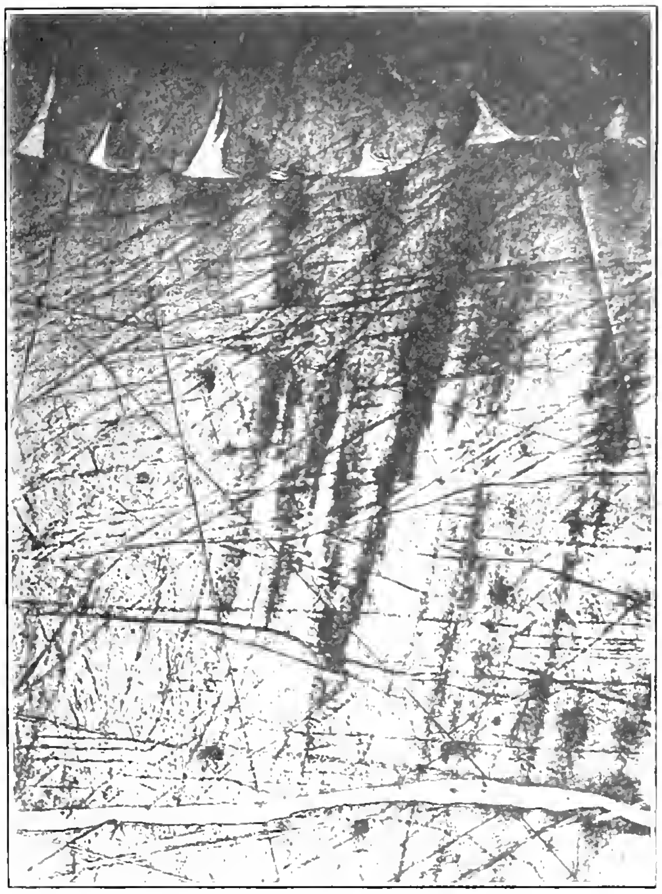


Fig. 5*b*.
× 50 diameters.

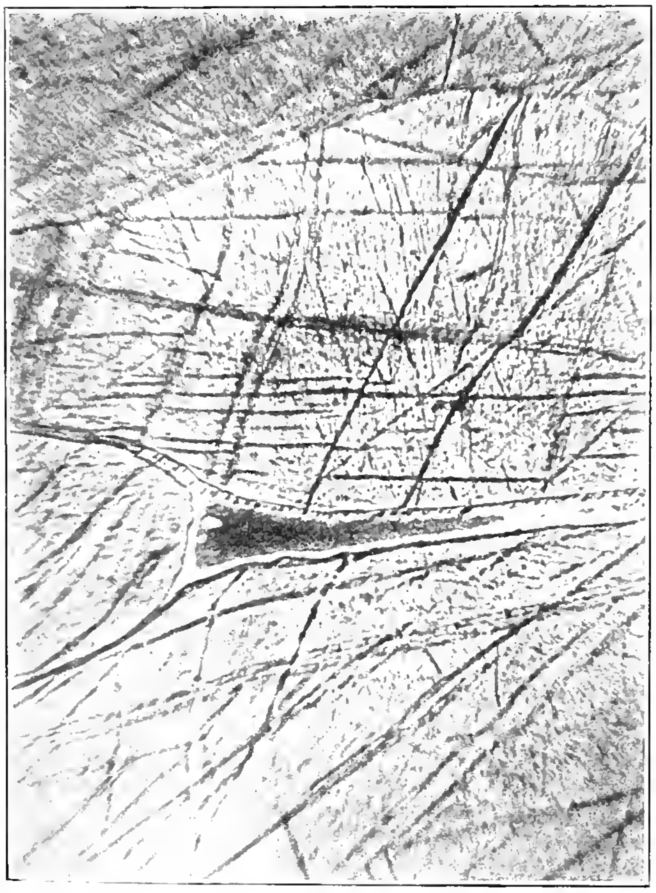


Fig. 5*c*.
× 80 diameters.

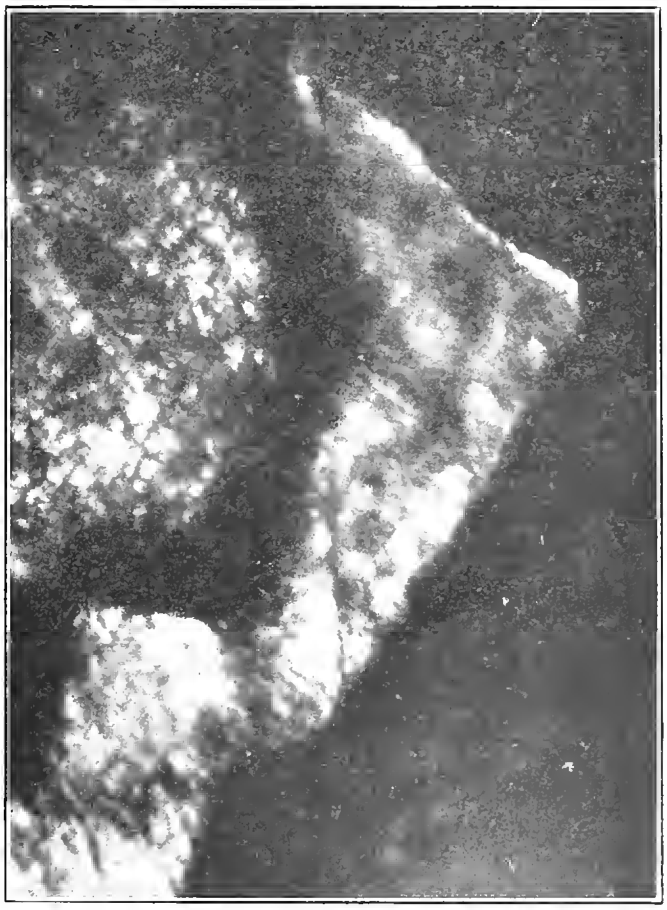


Fig. 5*d*.
× about 500 diameters.

Microphotographs of Sacramento meteorite.

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[PLATES 3–8.]

THE EFFECT OF PRESSURE UPON ARC SPECTRA.—No. 1. IRON

BY

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III. *The Effect of Pressure upon Arc Spectra.—No. 1. Iron.*

By W. Geoffrey Duffield, *B.Sc.* (*Adelaide*), *B.A.* (*Cantab.*), *Honorary Research Fellow in Physics at the Manchester University, Mackinnon Student of the Royal Society.*

Communicated by Professor A. Schuster, *F.R.S.*

Received July 4,—Read November 7, 1907.

[Plates 3–8.]

Contents.

Part I.

Part II.

As this paper is the first record of work undertaken with the large Rowland Grating in the Physical Laboratory of the University of Manchester, the occasion seems a fitting one for the description of the mounting of the instrument, which differs in several essential features from previously described systems.*

A detailed account of the scheme adopted for the adjustment of the apparatus is also given in the hope that it will be of service to those who may be confronted with a similar task. The papers of Ames and Kayser† on the adjustment of their own systems of mounting have been consulted and detailed acknowledgment will be found in the text.

PART I.

The Mounting of the Large Rowland Concave Grating.

The grating possesses 14,438 lines to the inch; the length of the ruled portion is 6 inches, its height 2 inches, and the radius of curvature of the concave metal surface upon which it is ruled 21 feet 6 inches.

Rowland's original system of mounting has, in general, been followed, though several important modifications have been introduced by Professor Schuster and by the constructor, Sir Howard Grubb. Two carriages, DD, fig. 1, which run freely upon two heavy girders, A and B, placed at right angles to one another, carry the grating and camera and are connected by a cross-beam, C, which is of such a length that the centre of the curved photographic plate is at the centre of curvature of the mirror. The slit is placed at the point of intersection of the two girders, which are shown in plan in fig. 1.

As the camera is moved away from the slit the grating moves towards it, the method of attachment being such that both turn with the cross-beam, which remains normal to the curved surfaces of the mirror and the photographic plate. With this disposition the spectrum should be in focus for all positions of the carriages along their girders. The mounting has been specially designed to make the various adjustments independent of one another and to ensure the stability of the carriages and their freedom from any constraint due to a possible twisting or sagging of the cross-beam.

The Girder for the Grating Carriage. (Fig. 1, A.)

This is a heavy cast-iron girder of ⊔ section, 20 feet 6 inches long, $6\frac{1}{2}$ inches high, 8 inches wide, whose upper edges have been machined, one to form a Λ and the other flat. These carry the wheels of the grating carriage. Kayser† had previously

---

* Ames, 'Phil. Mag.' (5), 27, 369, 1889. Kayser, 'Handbuch der Spectroscopie,' i., p. 473. Baly, "Spectroscopy," 'Textbook of Physical Chemistry Series,' p. 195. Adeney and Carson, 'Proc. Roy. Soc. Dublin' (1), 8, 711 (1898).

† 'Handbuch der Spectroscopie,' i., 473.

adopted a heavy carriage with four wheels, two of which were grooved to run on a rail, while a parallel wooden flat-topped beam served to support the other pair.

The Supports for the Grating Girder. (Fig. 1, F.)

Three cast-iron brackets are braced to the wall, and through their bases pass strong set-screws to afford a means for adjusting the plane of the girder and its height above the floor.

The Girder for the Camera Carriage. (Fig. 1, B.)

This is a heavy cast-iron girder of hollow rectangular section, 23 feet long, 18 inches high, and 8 inches wide, whose upper edges have been planed to form rails of the same shape and size as those of the grating girder.

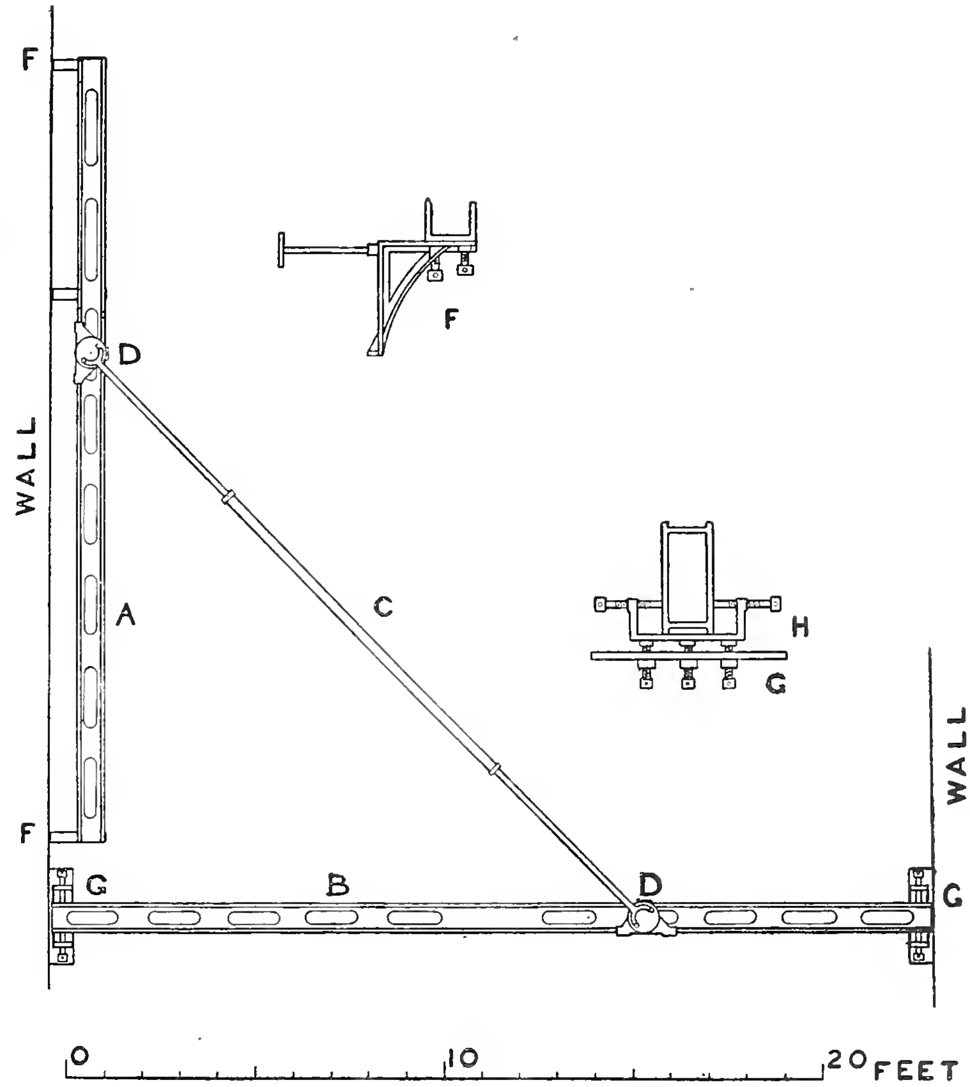

Fig. 1. General view of the mounting.

A. Grating girder.
B. Camera girder.
C. Cross-beam.
D. Carriages.
F. Bracket for grating girder.
G. Bracket for camera girder (built into the wall).
H. Cradle for camera girder.

The Supports for the Camera Girder. (Fig. 1, G and H.)

This girder spans the room from wall to wall, each end resting in a cradle, which stands upon a strong metal bracket built into the wall. The cradles are of cast iron of the pattern shown in fig. 1, H, and are 18 inches long, 6 inches wide, and $\frac{3}{4}$ inch thick; their sides are thickened at the top to provide sufficient metal for the two stout screws which serve to adjust the girder in a horizontal plane. Three set-screws with "tommyholes" passing upwards through the bases of the brackets support the cradles and regulate the height of the girder and the plane of its surface.

The Cross-beam. (Fig. 1, C, and fig. 2.)

This is a 4-inch tubular girder of wrought iron, as in Rowland's original arrangement,[*] but in this case constructed in three sections, of which the central portion is of slightly larger diameter than the ends, so that a telescopic adjustment of its length is possible. The sliding parts can be firmly secured by set-screws and by two flexible metal straps.

The method of attachment of the cross-beam to the grating and camera carriages, which is due to Sir Howard Grubb, obviates many of the defects of the earlier systems, which were not free from the constraint resulting from a too rigid connection.

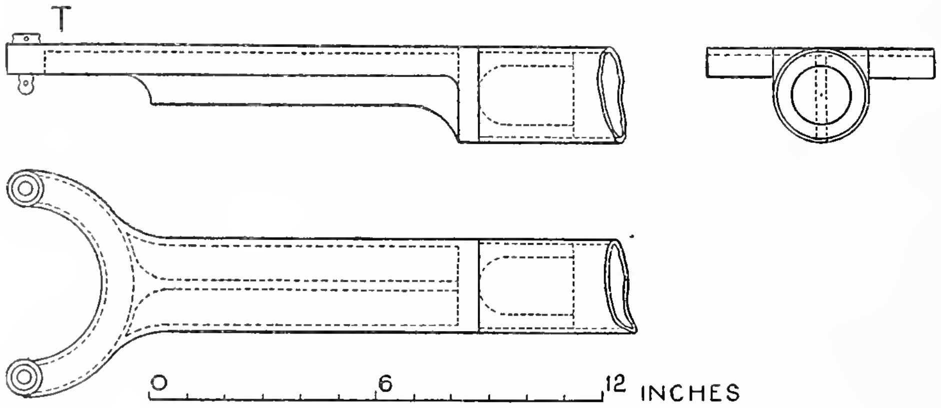

Fig. 2. The cross-beam ends.

Lugs were brazed on to the two ends of the cross-beam, fig. 2, and parallelism was obtained by turning them relatively to one another within the central tube. A second and more delicate means for obviating any constraint is provided by the set-screws T, which pass through the U ends of the lugs; these have rounded ends, and are turned until all four rest evenly in the hemispherical sockets VV, fig. 5, in the carriage mounting, and they are then held firmly in position by means of lock-nuts. This feature, combined with the stable form of the carriages, secures freedom from tilting of the grating and from any change of focus due to the sagging or twisting of the cross-beam.

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[*] Ames, 'Phil. Mag.' (5), 27, 369 (1889).

The Carriages for the Grating and Camera. (Fig. 3.)

Each carriage consists essentially of a heavy triangular casting supported upon three wheels, two of which are grooved to run upon the rail of the girder, while the third is flat. The whole is heavy, and stability is assured by the distance apart of the grooved wheels, which is 15 inches.

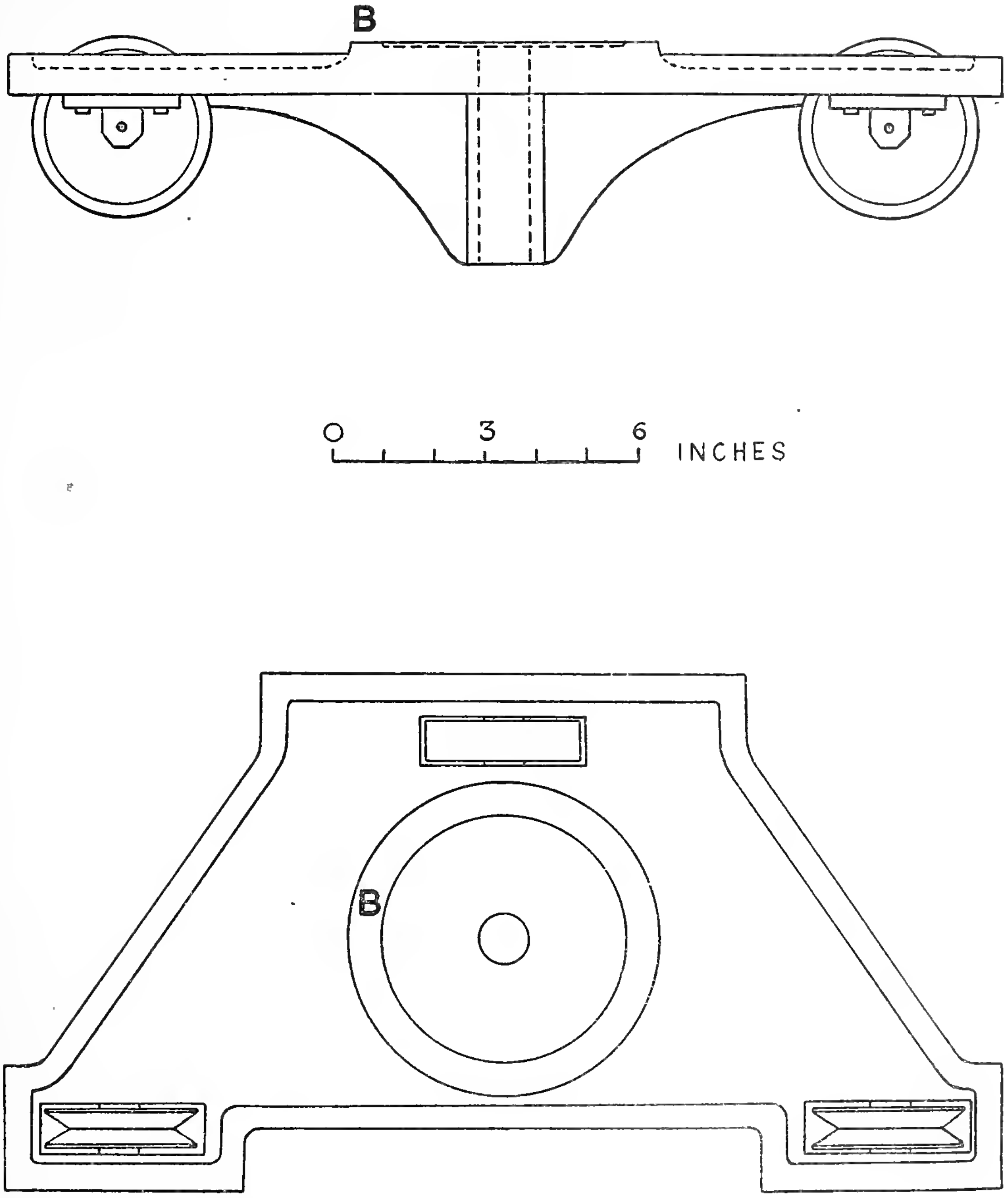

Fig. 3. The carriages for grating and camera.

Each end of the cross-beam, fig. 2, rests upon a casting (figs. 4 and 5, A), which turns upon a raised annular bearing surface (fig. 3, B) on the top of the carriage, and which has a solid steel pin, C, figs. 4, 5, to fit in a vertical hole drilled in the carriage itself. A cast-iron plate (F, fig. 4, E, fig. 5) furnished with a collar fitting over the top of this casting, to which it is firmly fixed by means of a set-screw, forms a table upon which rests either the grating holder or the camera box. The holes to receive the ends of the cross-beam are at opposite extremities of a diameter of the lower circular plate, and this provides that the distribution of the weight of the cross-beam upon the carriage is not altered when the cross beam is moved.

The Grating Holder. (Fig. 4.)

The grating itself is held in a metal box, the front of which has been cut away, and against this frame it is gently pressed by light springs, SS. The whole is mounted upon a circular brass plate $7\frac{1}{2}$ inches diameter, with a $\frac{3}{4}$-inch hole drilled at its centre, through which passes a short pivot fixed to a cast-iron plate, shaded in the diagram, to which the base plate can then be clamped—a fine adjustment, G, consisting of a flange attached to the upper plate held between two screws attached to the lower plate, allowing the correct angular position of the grating about its vertical axis to be accurately determined.

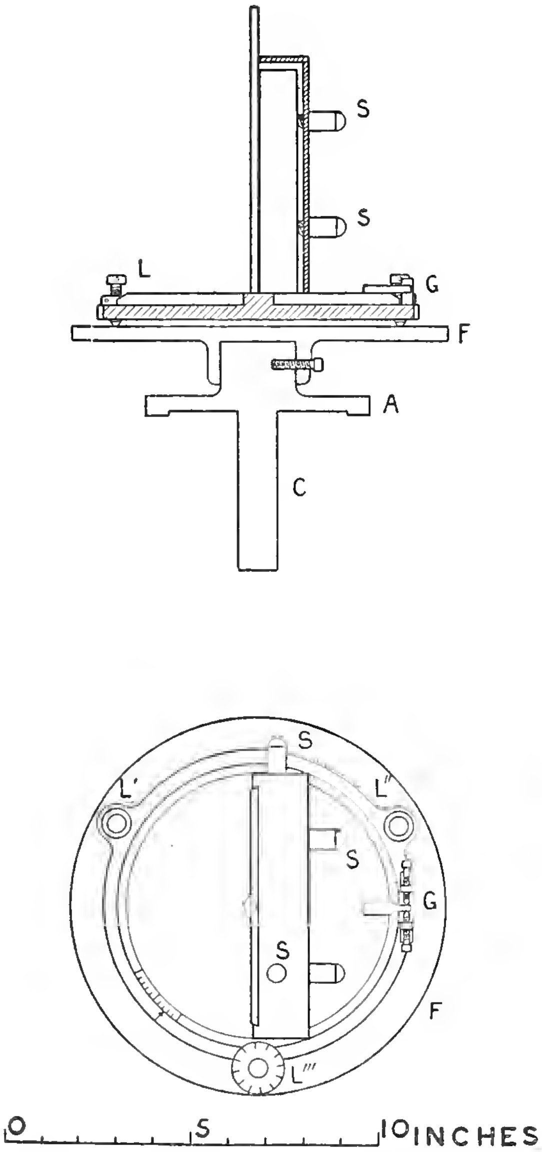

Fig. 4. The grating holder and grating table.

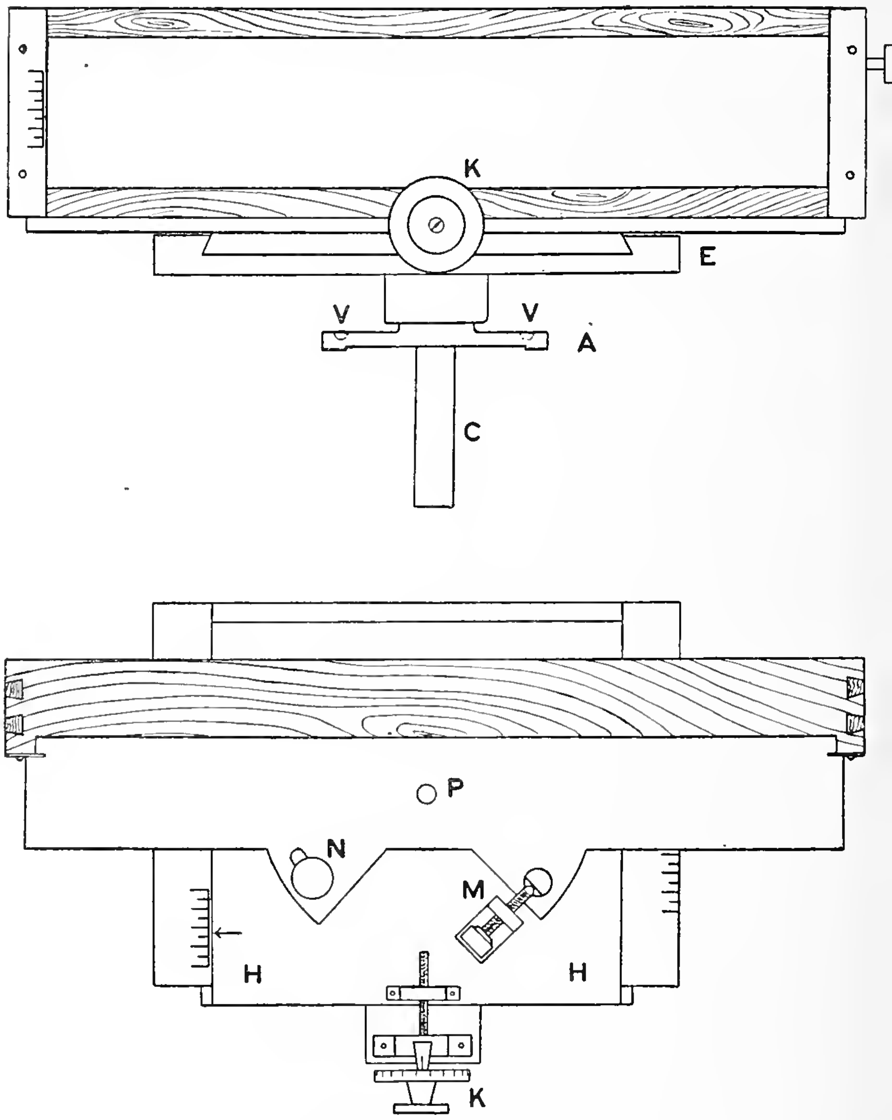

Fig. 5. The camera and its mounting.

Three levelling screws, L, on the lower plate fit into a hole-slot-plane system on the top of the grating table F, and by their means the height of the grating, its rotation about its normal through its centre and about a horizontal axis in its plane can be regulated. A divided head attached to these screws allows a record to be kept of their correct positions.

When not in use, the grating is protected by a glass plate which slides in vertical grooves in front of the ruled surface—this is replaced at other times by a black mask to cover the unruled portion of the mirror.

The Camera. (Fig. 5.)

The mounting of the camera box differs from that of the grating in having a rectangular metal plate, E, with grooves in which the base of the camera can slide, instead of the circular plate, F, to take the grating holder. The base of the camera is of brass and is capable of rotation about the pivot P in the sliding plate H, which is exactly below the centre of the photographic plate when that is in position in its dark slide.* The position of the pivot with reference to the camera carriage can be regulated by means of the screw K, which moves the sliding plate in its grooves.

M is a fine adjustment for turning the photographic plate about the pivot P, and when the correct angular position has been found the base plate may be fixed in position by means of the clamp N. M and N are not shown in elevation.

The dark slide moves in vertical grooves on the camera, so that several photographs may be taken upon the same plate. The plate, which is usually 20 inches by $2\frac{1}{2}$ inches, is pressed against rubber stops, which impart to it the necessary curvature.

The Comparison-shutter. (Fig. 6.)

This is now mounted apart from the camera box and is separately supported upon the grating girder to obviate any displacement of the spectra on the plate due to the operation of the shutter.* In the figure, R is a wooden block, heavily weighted with lead, to which is clamped the wooden grooved arm U, whose end carries a short length

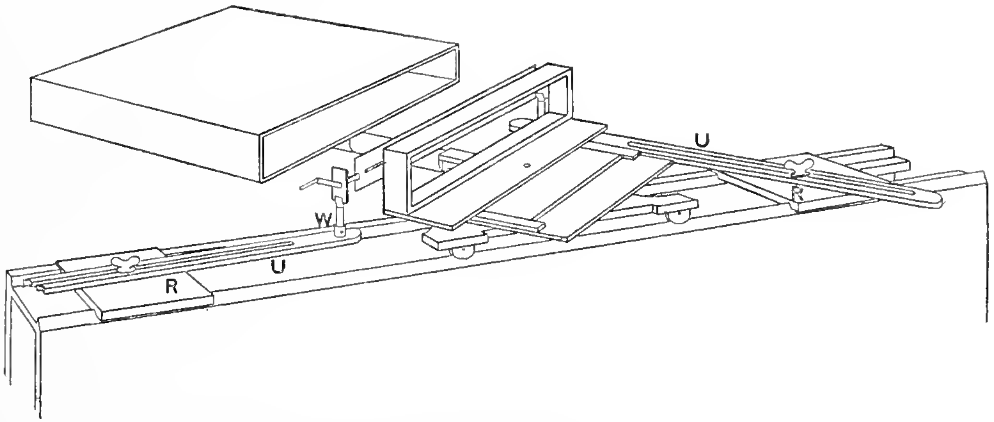

Fig. 6. The comparison-shutter and its support.

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* The writer is responsible for these and a few other minor modifications of the original design.

of $\frac{1}{2}$-inch brass tubing, W, into which fits a second tube of slightly smaller diameter, fixed to one end of the shutter, whose height is then capable of adjustment by sliding the tube up or down. It is then held in position by means of a set-screw.

The shutter itself is of the ordinary pattern, consisting in this case of two steel rules $\frac{1}{8}$ inch apart, soldered into end-pieces which are shaped to form the pivots about which it may be turned. It is placed as close as possible to the photographic plate; in fig. 6 for clearness it is shown some distance away. To screen the plate from diffused light, a light wooden box is supported on the cross-beam, and dark cloths attached to its sides are drawn over the camera box when the dark slide is in its place.

The Slit. (Fig. 7.)

This was designed by Sir Howard Grubb and made at the works of the Cambridge Scientific Instrument Company.

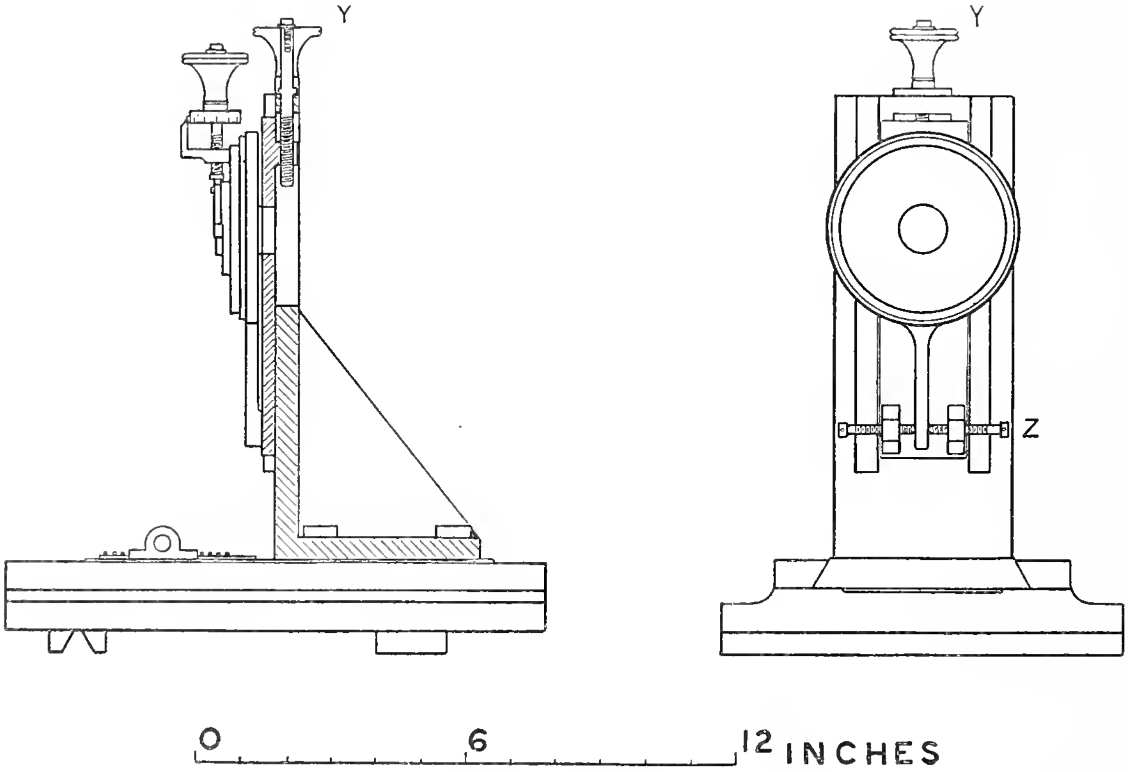

Fig. 7. The slit.

The requirements of a slit for use with a concave grating are that it be movable both along, and perpendicular to, the camera girder, that its height be adjustable, and that it be capable of rotation about its centre in its own plane.

The base of the mounting is grooved to rest evenly across the rails of the camera girder along which it may be moved, a scale and pointer indicating its position. Upon this base a plate carrying the slit slides in grooves, and the motion is controlled by a rack and pinion. The height of the slit is regulated by the screw Y, which passes through the top of the frame in which the slit itself slides. The jaws are held by a spring attachment to the circular metal plate, which can be turned in its own plane by the screws Z controlling the position of the lug attached to it.

Details of the mechanism by which the jaws are operated are not shown in the figure, but the system possesses the property of moving the knife-edges through equal distances as the width of the slit is altered, so that the position of its centre always remains the same.

The Grating Room.

The whole of the mounting is supported at such a level above the floor that it does not interfere with the floor space, which is therefore available for other purposes. At one end of the room a large platform has been erected, so that the camera can be easily manipulated, and a source of light placed in position and operated during the experiment.

Behind this platform are apertures in the wall through which sunlight can enter after reflexion from a heliostat. This can be placed on one of the ledges projecting from the outside wall, access to which is afforded by a balcony.

A ventilating chimney immediately over the source of light, usually an electric arc or spark, prevents obnoxious fumes from filling the room and injurious gases from reaching the grating surface. In addition, a screen of black cloth completely encloses this portion of the room and prevents stray light from affecting the plate. A hole in this screen permits the light to pass from the slit to the grating.

The room can be very perfectly darkened by means of blinds, and a double door permits access to or egress from it during the course of an experiment.

The electrical equipment of the platform consists of leads from the Corporation mains, from the storage batteries, and from the dynamo house, thus giving a wide range in the choice of voltage of both continuous and alternating current.

THE ADJUSTMENT OF THE LARGE ROWLAND CONCAVE GRATING.

The two carriages without their mountings were placed upon their respective girders and—

I. The grating girder* A, fig. 1, was so adjusted that the turned face of its carriage D remained horizontal for all positions along it. A spirit-level was laid upon the carriage, and the height of the four screws projecting upwards through the supporting brackets F altered.

II. The line of motion of the centre of the grating carriage was marked out.

A pianoforte wire, held at each end by a clamp, was stretched above the girder in

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* This girder was found to be considerably out of true alignment, so clamps were applied at intervals along its length to twist it until its edges were parallel and horizontal. The employment of a length of a lathe bed and saddle for the grating holder would obviate any twisting, and, I believe, possess many advantages over existing systems.

such a manner that as the carriage was moved the wire remained over the centre of the hole in which the pivot of the grating table turned.

III. and IV. Similar adjustments were made for the camera girder.

V. The line of motion of the centre of the camera carriage was adjusted perpendicular to the line of motion of the centre of the grating carriage.

KAYSER employed a theodolite to effect this, AMES the 3, 4, 5 method. The latter was adopted in the present case, and lengths of 4·5 m. and 6 m. were measured along the wires from their point of intersection, and a third wire, upon which a length of 7·5 m. was marked, was stretched across them, and the angle between the two girders altered by means of the cradle and side screws, fig. 1, G and H, until these marks coincided with those on the first two wires.

VI. The wires were removed and the slit placed at their point of intersection.

VII. An examination was made of the grating to ascertain on which side it threw the brighter spectrum of the second order; it was then placed in the grating holder, so that this spectrum should be employed.

VIII. The vertical bearing for the grating, ACF, fig. 4, was fitted into its carriage, and the grating in its holder placed in the hole-slot-plane system designed to receive it on the plate F. The base of the grating holder was made approximately horizontal by means of a spirit-level and the levelling screws L.

IX. The slit was moved vertically by turning the screw Y, fig. 7, until it was in the line of motion of the centre of the ruled space of the grating. The slit was illuminated by an arc and the light reflected from the grating received upon white paper surrounding the slit. The grating was moved to and fro along its girder, and the height of the slit altered until the centre of the reflected image remained upon the centre of the slit for all positions of the grating.

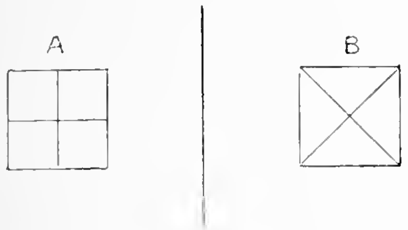
X. The vertical bearing for the camera, ACE, fig. 5, was fitted into its carriage and the camera fixed on it by means of the pin P. The spectrum was then adjusted horizontal and at the right height in the camera.

A piece of ground glass was placed in the dark slide in the camera, and by means of a scribing-block a mark was made on it at the height of the centre of the slit above the camera girder. The slit was illuminated and the spectrum observed on the plate. It was necessary to alter the screws L′ L″, fig. 4, to bring the spectrum to the required position. The camera was then moved along the girder and, as a change in the level of the spectrum was noticed, the screw L‴ was adjusted until the spectrum remained at the same height in the camera for all positions of the camera and grating on their girders.

The above operations insured the lines of the grating being vertical. The accuracy with which the face of the grating table had been turned was tested by rotating the grating about its axis and observing the position of the reflected image of the slit in the camera as it was moved along its girder. The centre of this image neither rose nor fell, so the mounting was considered satisfactory.

XI. The cross-beam was placed in position and (α) the grating was rotated until the pivot about which the centre of the plate turned was in the normal of the grating through its centre; (β) the length of the cross-beam was made equal to the radius of curvature of the grating mirror.

(α) was accomplished by the method described by Kayser of marking on a ground glass screen (a photographic plate which has been fixed for 10 minutes, without previous exposure, when it becomes almost transparent, is, after washing, a serviceable substitute) two small squares equidistant from a central line, and placing it in the camera with the central line directly above the pivot about which the camera box turns. A candle was held behind A, and its image observed with the magnifying glass in the square B while the grating was turned about its vertical axis by an assistant who operated the fine adjustment G. When the centres of the two crosses coincided, the central line lay in the normal to the grating.



(β) was effected by observing the image of A through the square B, as before, and racking the camera box backwards and forwards by means of the screw K, fig. 5, until all parallax disappeared and no motion of the eye caused the image of A to move within the square B. This determination was a matter of some difficulty and delicacy, and several independent observations were made by different observers. The adjustments of the mounting necessary for (β) require the displacement of the centre of the plate from its true position above the pivot, but the distance through which the plate-holder was moved was noted, and the cross-beam was lengthened or shortened by the amount requisite to restore the plate to its correct position. The telescopic adjustment allows this to be easily performed.

XII. The slit was adjusted parallel to the lines of the grating.

The slit was rotated in its own plane about its centre by turning the screws Z, fig. 7, and with the usual method of illuminating the slit many photographs were taken on a small plate placed immediately over the pivot P, fig. 5. The spectrum of the iron arc was employed, and that disposition of the slit giving the best definition was chosen.

A simple test, due to Kayser, of the accuracy of this adjustment is to cover the middle of the slit to make it equivalent to two short slits separated by an opaque interval; a photograph taken with this disposition will show two spectra whose lines are drawn out by the astigmatic property of the grating to nearly meet in the centre. When the slit is parallel to the rulings, the two portions of the slit give a continuous line, otherwise the two lines are slightly displaced.

The fineness with which the ends of spectral lines (*e.g.*, those of the iron arc) are pointed, and the precise similarity of their two ends, is also a good gauge of the accuracy of this adjustment.

XIII. The camera was adjusted so that the centre of the grating lay in the normal to the plate through its centre.

The method adopted for accomplishing this was to take photographs of the iron arc spectrum in the usual way, on three small plates placed at the two ends and at the centre of the dark slide, between the exposure of each set the camera was turned slightly by means of the screw M, fig. 5, about the pivot P, and the disposition of the camera giving equally good definition for the ends as for the middle was selected. AMES describes a convenient method for obtaining a rough approximation: a piece of plate glass having been fixed to the face of the camera box, a candle is held on the girder near the grating, and the camera turned until the flame and its image come into line.

XIV. The adjustment necessary to correct for changes of temperature was made.

Changes of temperature prevent the spectrum from remaining in focus continually, since the focal length of the grating mirror and the length of the cross-beam are liable to alteration on this account.

The first care has been, therefore, to keep the temperature of the grating room as even as possible, and after this to move the slit towards or away from the grating, according as the temperature rose or fell, the best position at each temperature being found by trial photographs. A scale denoting the correct positions of the slit for different temperatures was in this way constructed and has been found to work well; the necessary motion of the slit is approximately 1 millim. for one degree Centigrade. Since the expansions of the grating and the cross-beam are unequal in their effects on the focus, at some temperatures the best definition is rather better than that attainable at others.

The expansion of the grating also affects the dispersion in the spectrum to an unsuspected extent. A simple calculation shows that $\delta\lambda/\lambda$ is equal to α, the coefficient of linear expansion of the grating. For $\lambda = 5000$ Å.U., and $\alpha = 0{\cdot}00002$ for speculum metal, $\delta\lambda = 0{\cdot}1$ Å.U. for a change in temperature of one degree Centigrade. The necessity for regulating the temperature of the grating room at once becomes apparent.

I have pleasure in acknowledging the services of Mr. T. ROYDS, B.Sc., who assisted me in making these adjustments. My indebtedness to the papers of AMES and KAYSER has already been expressed; to Professor KAYSER I am also grateful for his criticism of photographs obtained with this grating.

PART II.

THE EFFECT OF PRESSURE UPON THE SPECTRUM OF THE IRON ARC.

1. *Preliminary.*

Most intimately connected with the problem of the influence of pressure upon arc spectra are the names of HUMPHREYS and MOHLER,[*] who in 1897 published a full account of their investigations in this subject. They formed an arc between metal or cored carbon poles within a strong metal chamber furnished with a window, through which the arc was observed. Air or other gases could be pumped into the apparatus, and it was found that with an increase of pressure the spectrum underwent a change, the lines in general becoming broader and being slightly displaced towards the region of longer wave-lengths. Up to 14½ atmospheres, which was the highest pressure reached, the displacement of the lines for all the metals investigated was found to be directly proportional to the pressure, and a subsequent photograph of the spectrum of iron, which HUMPHREYS obtained at 37 atmospheres in 1905,[†] tended to confirm this.

MOHLER[‡] extended the work to pressures lower than one atmosphere, and the linear relation was still found to hold. In 1906, ANDERSON[§] obtained a photograph of the iron arc at a pressure of 30 atmospheres.

The present research was begun by the writer in November, 1904, with the object of extending the work of HUMPHREYS and MOHLER to still higher pressures, and two sets of photographs of the direct-current iron arc have now been obtained under pressures ranging from 1 to 100 atmospheres, the surrounding medium being in all cases air. This work was greatly facilitated by the preliminary work of HUTTON and PETAVEL,[||] who in 1903 published the results of a research made with the same pressure apparatus and a 1-m. Rowland grating. The possibility of photographing the spectrum from an arc under pressures up to 100 atmospheres was demonstrated, as well as the probability of a successful use of the pressure apparatus in conjunction with a spectroscope of the highest dispersive power.

In August, 1906, the writer[¶] exhibited to the British Association photographs of the arc spectrum of iron taken with the 21½-feet grating under pressures varying from 1 to 101 atmospheres.

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[*] HUMPHREYS and MOHLER, 'Astrophysical Journal,' VI., 169, 1897; also 'Astrophysical Journal,' III., 114, 1896; IV., 175, 1896; IV., 249, 1896; for data published during the progress of their work.

[†] HUMPHREYS, 'Astrophysical Journal,' XXII., 217, 1905.

[‡] MOHLER, 'Astrophysical Journal,' IV., 175, 1896.

[§] ANDERSON, 'Astrophysical Journal,' XXIV., 221, 1906.

[||] HUTTON and PETAVEL, 'Phil. Mag.,' 6, p. 569, 1903.

[¶] DUFFIELD, 'Brit. Assoc. Report,' York, p. 481, 1906.

Of the results obtained by HUMPHREYS and MOHLER, the following are tabulated as being pertinent to the subject of this paper :—

(1) The Shift is proportional to the excess of pressure above one atmosphere, and takes place towards the red end of the spectrum.
(2) The Shift is different for different elements.
(3) The Shift differs for different groups of lines in the spectrum of any one element.
(4) The Shift of lines belonging to the Second Subordinate Series is twice the shift of those belonging to the First Subordinate Series, which is itself twice that of those belonging to the Principal Series, *i.e.*, the shifts are in the ratio 4 : 2 : 1.
(5) The Shift of some iron lines is three times the shift of other lines in the same Spectrum.
(6) The Shift is proportional to the wave-length for lines of the same series.
(7) A few lines showed no broadening.

The effect of pressure on the spark discharge in liquids and gases has now been investigated through a wide range by HALE,[*] HALE and KENT,[†] LOCKYER[‡] and ANDERSON,[§] and it has been shown that the effect of self-induction and capacity in the spark-circuit also affects the frequency of the vibrations ; it is not, therefore, possible to compare quantitatively the results of their investigations with those of HUMPHREYS and MOHLER, who used a direct-current arc.

2. *The Apparatus.*

The pressure cylinder, Plate 1, figs. 1 and 2, was designed by Mr. J. E. PETAVEL, F.R.S., and constructed by Mr. CHAS. W. COOK, of the Manchester University Engineering Works. This cylinder was used by HUTTON and PETAVEL for their 'Preliminary Note on the Effect of Pressure on Arc Spectra,' to which reference has already been made.

The pressure apparatus consists of a cylinder of drawn steel, fig. 8, 2 feet long, 3 inches internal and 5 inches external diameter, lined inside with brass $\frac{1}{16}$ inch thick ; to the top and bottom heavy flanges are screwed, and to these are bolted the covers which carry the arrangement for feeding the arc mechanically. The rods passing through the covers are screwed where they pass through the insulated plates at the top and bottom of the apparatus, and these are operated by the hand-wheels shown in the diagram. The current passes through the feed-rods to the electrodes which are attached to their extremities, and which form an electric arc opposite a

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[*] HALE, 'Astrophysical Journal,' XV., 132, 1902.

[†] HALE and KENT, 'Astrophysical Journal,' XVII., 154, 1903 ; and 'Publications of Yerkes Observatory,' Vol. III., Part II., 1907.

[‡] LOCKYER, 'Roy. Soc. Proc.,' LXX., 31.

[§] ANDERSON, 'Astrophysical Journal,' XXIV., 221, 1906.

window in the side of the cylinder, made of glass ground into the shape of a truncated cone, and so fitted into its seat in the cylinder that an increase of pressure tends to make the joint tighter. The whole cylinder is surrounded by a water-jacket through which water circulates and carries off the heat generated by the arc. Details of the design are described elsewhere,* and fig. 8 merely indicates diagrammatically the essential features of the apparatus. The stuffing-boxes in the covers perform the function of insulating the electrodes from the sides of the cylinder, besides that of permitting a vertical motion of the feed-rods without escape of gas.

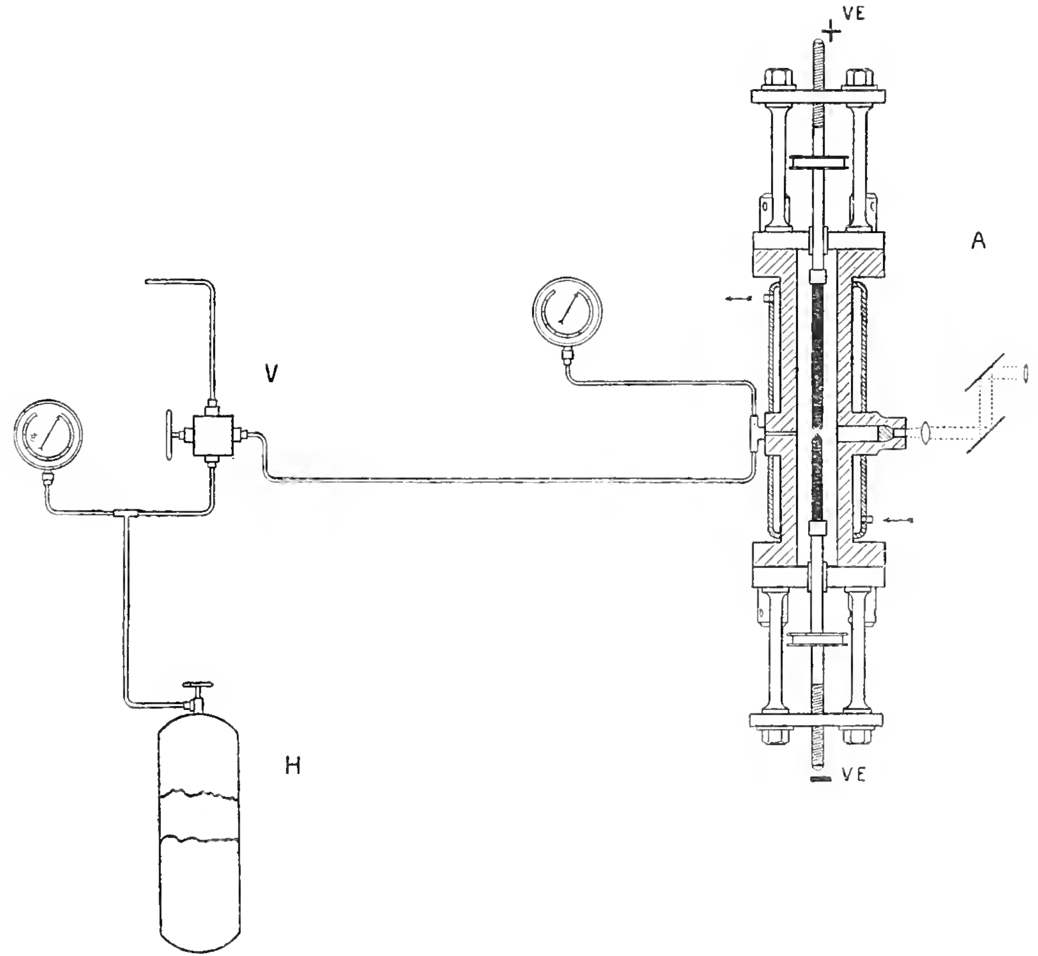

Fig. 8.

The maintenance of the highest pressures for long periods without appreciable leakage testifies to the excellence of Mr. PETAVEL's design. The writer here desires to express his indebtedness to Mr. PETAVEL for the use of the pressure cylinder and connections, and for valuable advice upon their management.

For the production of pressure within the cylinder the gas holder H, fig. 8, which was filled with air at a pressure of 120 atmospheres, was placed in communication with the pressure cylinder through the valve V, which could also afford a means for the escape of the gas from the pressure cylinder A to the outlet pipe. Pressure gauges indicated the pressures in the gas holder and in the cylinder.

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* HUTTON and PETAVEL, 'Electric Furnace Reactions under High Gas Pressures,' read Royal Society, March 7, 1907.

As there was a certain amount of risk of the window being blown out, it was usual to operate the feeding of the arc from a little distance by ropes passing round the pulleys on the covers ; save, however, for some slight chipping of the inner surface, due to straining, the window has remained intact.

3. *The Illumination of the Slit.*

During the present research, in which the large dispersion of the 21-feet 6-inch Rowland grating was employed, it was found that extremely long exposures were required, and a number of unsuccessful attempts were made before a photograph of the spectrum under pressure was obtained. It became, therefore, most important to obtain the maximum illumination of the grating from the light passing through the window of the pressure cylinder.

The system of lenses employed is shown in the diagram : lenses K and L are at their focal distances from the arc and slit respectively.

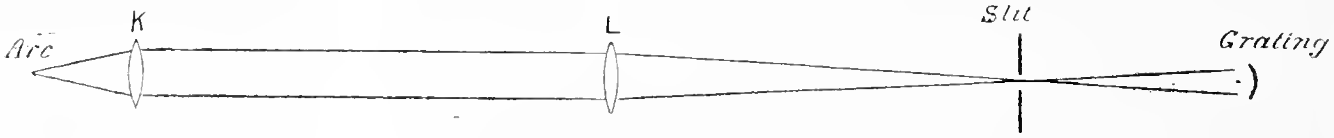

Fig. 9.

The cone of light from the lens L passes through the slit, and a little more than just fills the grating ; this is not the usual arrangement, but the conditions differ from those contemplated by SCHUSTER,* who finds that the conditions for maximum uniform illumination are fulfilled when the angle subtended by the lens is four times that subtended by the grating at the slit. In the present instance the original cone of light is limited by the window in the cylinder, and the most efficient use is made of it by refracting it into the slit by a lens which subtends at the slit the same solid angle as the grating. The central maximum of the diffraction pattern for each ray then falls upon the grating, ensuring a sufficiently (but not perfectly) even illumination of its surface, and the loss of very little light.

Dealing with the concave grating, the size of the image of the arc on the slit is of some influence on the intensity of the spectral lines, because the astigmatic properties of the ruled surface serve to partially integrate the effects from different parts of the slit. In a prism spectroscope this is not the case, and the size of the slit does not affect the intensity of the lines. The lens K was therefore introduced in order that the image of the arc should just fill the slit ; in this way the intensity of the illumination of the slit was not altered, since the angle subtended by the lens L at the slit remained constant, but the total quantity of light received over the area of the slit was then a maximum.

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* A. SCHUSTER, 'Astrophysical Journal,' XXI., p. 209, 1905.

4. *The System of Mirrors.*

It was found by some preliminary work that special means were essential for continually adjusting the image of the arc upon the slit; as soon as the air in the cylinder was compressed the arc became unsteady, and moved about the ends of the electrodes in an uncertain manner. Without a means of training the image on to the slit only a very small proportion of the length of exposure was effective, but with the apparatus to be described it was easy to follow the movements of the arc, and to ensure its almost continual focussing on the slit.

Two mirrors were silvered and polished on the surface, and fitted into frames which held them at an angle of 45° with the horizontal; the upper was fixed with its centre in the line joining the centre of the grating with the centre of the slit. The second was placed 4 inches below the first, opposite the window of the pressure cylinder, and could be moved parallel to itself by means of the rack and pinion shown in fig. 10.

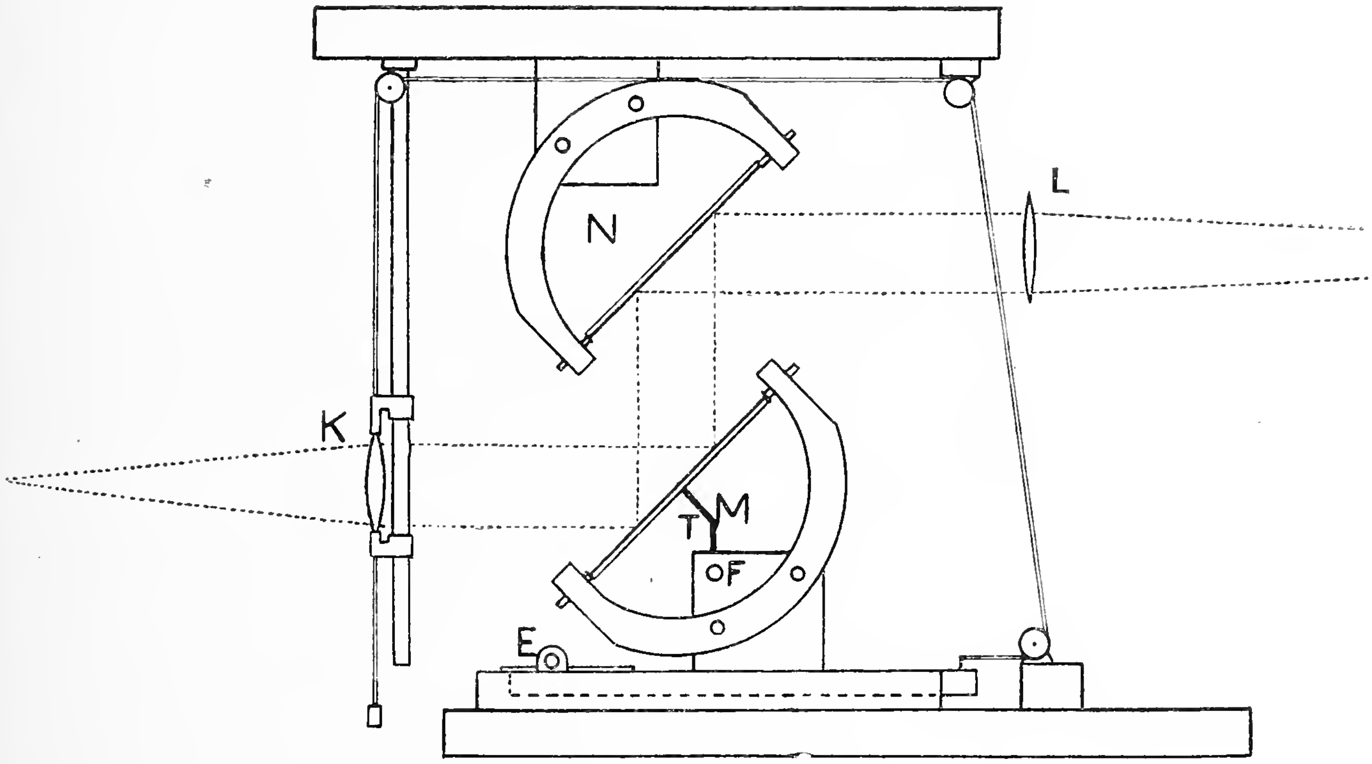

Fig. 10. Arrangement of mirrors.

Vertical displacements of the arc from its central position, caused by unequal consumption of the electrodes or unequal feeding, were counterbalanced by this motion. If we confine our attention to the bundle of rays symmetrical about a horizontal ray and for the moment neglect the lens K, we see that a lowering of the arc (which occasions a lowering of the position of the spot of light received upon the upper mirror) may be counterbalanced by moving the mirror M parallel to itself away from the arc. This restores the reflected beam to its original position on mirror N; similarly, when the arc is higher than usual, the re-adjustment is effected by moving the mirror M forward.

Without the lens K, the direction of the beam of light passing through the window would change as the arc shifted its position, and it would be necessary to alter the angles of the mirrors and the position of the lens L in order to keep the image in focus on the slit, but the lens K has been arranged to move up or down just as much as the arc moves up or down, by means of the system of pulleys shown in the diagram, which ensures the vertical motion of the lens being equal to the horizontal motion of the mirror M; when M moves towards the arc, L is pulled up, and *vice versâ*. The ray passing horizontally through the window thus always proceeds through the centres of the second lens, the slit and the grating, and all danger of a fictitious shift due to want of centrality is obviated. When the arc fluctuates horizontally round the poles the image is brought back upon the slit by turning the mirror M about its pivots; the motion required is very small and the adjustment can be made rapidly enough for an experienced operator to keep the image of the arc almost continually in position. Since the arc and slit are in the focal planes of their respective lenses the image is always in good focus.

The turning of the mirror about its long axis is effected by the screw F, which presses against a projection T from the back of the frame holding the mirror, a spring keeping F and T in close contact. Universal joints were attached to the ends of E and F, and long handles provided, fig. 2, Plate 3, so that the assistant whose duty it was to keep the image on the slit was not too close to the window.

This mirror system was designed by the writer and constructed by Mr. GRIFFITHS in the workshop of the Physical Laboratory. To it the success in photographing the spectrum of the arc under high pressures is largely due.

5. *General Arrangement of the Apparatus.*

Plate 3, fig. 2, shows the cylinder in position in front of the Rowland grating spectroscope, the slit of which is to be seen at the right of this photograph standing on the cast-iron girder along which the camera carriage runs. The cylinder is mounted on a swinging jib turning on the vertical axis at the left of the picture, so that it can be moved out of position when the grating is required for other work. A screw-jack at the base of the jib allows the cylinder a vertical range of adjustment of about 6 inches.

On a level with the window is the lens which slides in vertical grooves, and beyond it the arrangement of mirrors is to be seen. These were operated by an assistant who stood at some distance from the apparatus and worked them by means of the two wooden handles. The second lens is held in the clamp of the retort stand and was accurately adjusted in line with the centres of the slit and the grating.

The ropes for operating the mechanical feeding of the arc were not in position when the photograph was taken, nor is the auxiliary shutter shown; this latter was fixed beyond the slit, so that its operation caused no jarring to the mounting of the grating.

The rubber pipes for supplying the jackets with water may be seen, one in front at the bottom of the cylinder, and the other behind it at the top. Above the cylinder a ventilating chimney serves to carry off any noxious vapours which might otherwise escape into the room, and a block and tackle arrangement facilitates the removal of the cylinder covers.

6. *Precautions necessary in taking the Photographs.*

The object of the experiments was the direct comparison of the spectrum of the iron arc when subjected to high pressures with the spectrum emitted under ordinary conditions. To facilitate the examination of the relative positions of the lines in the two cases it was desirable to photograph the two spectra in as close proximity as possible, and for this purpose the usual form of comparison-shutter was adopted. This caused the central strip of the plate to be exposed to the arc under pressure, and above and below this strip the comparison spectrum to be photographed; or *vice versâ*. The shutter is described in Part I., p. 117. The dispersion of the second-order spectrum (1 millim. = 1·3 Å.U.) was employed in this research.

The following precautions were taken to insure the freedom of the photographs from any fictitious displacement of the lines :—

1. To prevent jarring of the camera when the shutter was operated, the latter, which was originally fixed to the camera box, was detached from it and separately supported, as already described.

2. To make sure that the conditions were the same for the two different positions of the shutter, some photographs were taken with the pressure spectrum within the central strip and others with the comparison spectrum in the centre. No systematic difference was found between the two.

3. To insure the absence of an apparent shift due to the illumination of the grating being different for the two exposures, the arrangement of mirrors and lenses already described was adopted. Since the mirror N and the lens L, fig. 10, were fixed, the light always passed through the lens L in the same direction when the image of the arc was in focus on the slit. This is the necessary condition for constant distribution of illumination over the grating. That no conditions might be different for the two exposures, the comparison spectrum was taken from the same metallic poles within the cylinder.

4. As a fictitious displacement of the lines might also be caused by a change in temperature of the grating (see Part I., p. 122), a careful watch was kept upon a thermometer placed near it. For some weeks it was found impossible to take photographs on account of the fluctuations of the temperature, of which complete records were kept, and, although one or two reliable photographs at low pressures were taken at night towards the end of 1905, it was not until the Spring of 1906 that the temperature of the room settled down sufficiently for long exposures to be made. a

long period of rainy weather proving of great service in the prosecution of this research.

5. To have a means of ascertaining whether the photographs taken were reliable, the comparison spectrum was invariably photographed by a divided exposure ; the spectrum of iron arc at atmospheric pressure was taken immediately before and also immediately after the pressure exposure, and the positions of these two spectra were carefully examined. Any disturbance of the apparatus or continuous change in temperature during the experiment could thus be discovered, and all plates in which the lines were not accurately coincident were rejected.

7. *The Behaviour of the Iron Arc under High Pressure.*

Under ordinary conditions the iron arc was maintained almost as easily as the carbon arc, but an increase of the pressure of the air surrounding it caused its management to become more difficult. The disturbed area on the positive pole from which the arc sprang was in constant motion over the surface of the turbulent molten mass, and luminous metallic vapour was constantly expelled in all directions. These convection currents rendered the arc very unstable, and at a pressure of only 10 atmospheres it was difficult to maintain it for more than half a minute on account of the tendency of these flames to blow it out.

At higher pressures the life of the arc became shorter, and at 50 atmospheres the exposure consisted of a series of flashes of not much more than a second's duration, the maximum length of the arc being then about 2 millims. For the first pair of iron poles, between 300 and 400 flashes were required to affect a photographic plate, so it was necessary to prolong the process of striking the arc and withdrawing the poles for a period of from 40 minutes to one hour. Up to 50 atmospheres a workable scale of exposures was to open the shutter for the same number of minutes as the number of atmospheres employed, but for pressures between 50 and 100 atmospheres it was not necessary to increase the exposure beyond one hour.

A second set of photographs, Set B, was taken with another pair of iron poles, and these proved much more satisfactory, as the arc lasted much longer at all pressures, at the highest pressure only 8 to 12 minutes exposure being required, and this rendered the plates less liable to fogging from stray light in the room. The two sets of photographs are subsequently referred to as Sets A and B.

The specimens of iron bar were obtained from the same source in the two cases.

The length of the exposure necessitated the use of a wider slit than would otherwise have been employed; this was decided upon experimentally by taking a series of photographs of the iron arc at ordinary pressures with different widths of slit and choosing that aperture at which the definition just remained good—the series showed that the definition decreased gradually to a point at which it suddenly became bad : a reasonable margin for accidental alterations was allowed, and the slit width chosen gave a definition sufficiently good for the finely reversed portions of the lines *b*3, *b*4, *c*0, &c., Plate 4, to remain quite clear. The width was found to be 0·022 millim., a larger value than that required for perfect definition, viz., 0·007 millim.

W. E. WILSON[*] and WILSON and FITZGERALD[†] have observed the changes in the temperature and brightness of the carbon arc in different gases under pressures varying from 1 to 20 atmospheres. No very concordant results were obtained, as the absorption of the light by the vapour in the long observing tube was considerable and fluctuating, but the evidence tended to show that with the carbon arc there is no increase in the intensity of the light emitted from the crater when the pressure of the surrounding gases, whether oxygen, nitrogen, or hydrogen, is increased.

During the course of the present experiments notes were made of the apparent intensity of the light at each pressure, and, according to visual observations, the brilliance of the image thrown upon the jaws of the slit increased gradually with the pressure until at 100 atmospheres it became painful to the eyes to observe it, the brightness apparently increasing more rapidly after 50 atmospheres than between 1 and 50 atmospheres.

It is to be remarked that with this increase of brightness there is little concomitant decrease in the necessary time of exposure. As the pressure was increased the spectral lines became very much wider and more diffuse, and in some instances were spread out over 15 Ångström units; consequently, though there is an increase in the intrinsic brightness of the arc, the fact that the area over which the energy of vibration is spread is increased in a greater proportion, results in the intensity of the radiant energy received upon the photographic plate being less than that received when the total amount of light is less and the energy concentrated into narrow lines.

The city mains at 100 volts were used as the source of supply, a reduction being effected by a resistance frame. The current in the arc varied from 12 to 20 ampères; this could not be measured accurately on account of the intermittent nature of the arc, nor could a higher voltage than 50 be used across the terminals, because at the moment of striking it a short circuit through the molten metal was produced, and the wiring of the building was not capable of taking more than 30 ampères.

An interesting phenomenon, to which reference will be made later (p. 153), was observed in connection with the coating of the window with a black deposit derived from the arc; this was very troublesome between 1 and 20 atmospheres, and it necessitated the removal and cleaning of the window after each exposure, but between 20 and 30 atmospheres this ceased, and from 30 to 100 atmospheres the window remained perfectly clear. It may be that the particles shot off from the arc cannot, at high pressures, penetrate the dense envelope of air, or it may be that the hot vapours extend right from the arc to the window and consume the metallic particles. The former is the more acceptable hypothesis, since the latter condition can scarcely hold

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[*] WILSON, 'Astrophysical Journal,' II., 213, 1895; 'Roy. Soc. Proc.,' 58, 174, 1895.

[†] WILSON and FITZGERALD, 'Astrophysical Journal,' V., 101, 1897; 'Roy. Soc. Proc.,' 60, 377, 1896.

at pressures of 95 and 100 atmospheres when the arc is of too short duration for the formation of the necessary quantity of vapour.

8. *General Features of the Results.*

1. *The Broadening of the Lines.*—It will be seen from the photographs accompanying this paper that the first obvious effect of an increase of the pressure of the gas surrounding the arc is the *broadening of the lines.*

Under a pressure of three atmospheres, Plate 4, No. 1, the widths of all the lines are appreciably increased, and under higher pressures this becomes still more marked. The width is too dependent upon the length of the exposure and the nature of the photographic process* for more than a general idea of the broadening to be obtained from the photographs, but it will be seen that the lines widen and become more diffuse as the pressure is increased, and that *the amount of broadening is different for different lines*; those that reverse strongly are spread out over a large range (*e.g.*, lines marked *b*3, *b*4, *c*0, *d*0, *d*2, &c.), while others remain comparatively sharp (*b*1, *b*2, *c*1, *c*2, *c*3, *d*1, &c.), though these are not nearly as fine under high pressure as they are under one atmosphere. It is in general true that the lines that are originally strong are the ones that are most broadened under pressure.

The broadening of most lines is unsymmetrical, being greater towards the region of greater wave-length; the following lines illustrate this well: 2, 3, *d*3, *f*1, *f*2, Plates 4, 7 and 8. Those that reverse easily, *b*3, *b*4, *c*0, *d*0, *d*2, &c., however, appear to broaden almost symmetrically, and so do the lines already mentioned as remaining comparatively sharp at high pressure. In no instance has a line been found with a greater broadening on its more refrangible side. It should, however, be remarked that there is invariably some broadening towards the violet, but not always to the same extent as towards the red end of the spectrum. The phenomenon of broadening may be studied in Plate 5, fig. 1, in which, however, the exposures are not quite comparable.

2. *The Displacement of the Lines.*—A careful study of the photographs, Plate 4, reveals the fact, first discovered by HUMPHREYS and MOHLER, that there is a slight *displacement of the lines towards the red end of the spectrum as the pressure of the vapour about the arc is increased.* At low pressures it is not quite definite that this phenomenon is not due to an unsymmetrical widening of the line, but the photographs taken at high pressures dispose of this objection, because several lines are then displaced so much that they are quite clear of their comparison lines. The lines *f*1, *f*2, *f*3, at 100 atmospheres, No. 9, Plate 4, show this well, and it is emphasized in the enlargement, Plate 8, and in Plate 6, fig. 1, in which the shift of *d*3 at 100 atmospheres is specially remarkable; the lines 2, 3, *a*1, Plate 7, though not displaced quite as much, also testify that the displacement is a real phenomenon.

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* The photograph at 10 atmospheres (No. 2) is over-exposed in comparison with the other spectra.

The question of the magnitudes of the displacements are discussed under a separate heading.

3. *The Reversal of the Lines.*—In the region of the spectrum examined, several lines are reversed at ordinary atmospheric pressure, such are *b*3, *b*4, *c*0, *d*0, *d*2, &c., but under increased pressure the reversals become stronger and other lines originally unreversed exhibit the phenomenon; such are *b*1, *c*1, *d*1, *f*1. It thus follows that *the immediate effect of pressure is to increase the number and intensity of the reversals.* But at a pressure of about 25 atmospheres for Set A, the maximum tendency to reverse is reached, and *above 25 atmospheres the reversals decrease in number and generally in width.* For Set B, the maximum intensity of the reversals occurs at 20 atmospheres; it may also be seen from Table II. that the reversals are more numerous at 10 atmospheres than at 15 atmospheres. In Plate 5, fig. 1, in which the spectrum photographed at 100 atmospheres pressure is not exposed as much as the other spectra under pressure, the lines *b*3, *e*3, *e*4, are reversed most strongly at 25 atmospheres; a careful examination of the original negatives under a high magnifying power is, however, necessary for the detection of the fine reversals of *b*1, *c*1, &c. A few lines remain strongly reversed even at the highest pressures reached, *c*0, *d*0, *d*2, *e*1.

Some reversals are symmetrical, *i.e.*, the absorption line is in the centre of the bright emission line, see lines *d*0, *d*2, Plate 6, fig. 1; others are unsymmetrical, see line *e*3, Plate 6, fig. 2. A separate section, p. 152, is devoted to the discussion of this phenomenon.

9. *Measurement of the Photographs.*

The plates were measured on a Kayser measuring machine in which they are firmly attached to a table which travels on a fine screw in front of a fixed eye-piece containing the cross-wires; depressing a key prints the reading of the scale on a tape and enables several measurements to be made without moving the eye from the instrument. The shifts were measured by causing the line under pressure and its comparison line to travel in succession past the double wire of the eye-piece, the key being depressed as the most intense portion of each spectral line came between the double threads; the setting on the broadened portion of the line was generally made first, because it was then found easier to decide upon its most intense portion. In some few cases in which the line was abnormally broad, the film was pricked under a low-power magnifying glass which enabled the position of maximum intensity to be more easily gauged, and the position of this dot was then measured. Some of the plates were taken with the pressure spectrum within the comparison spectrum, but most of them in the reverse manner; no important differences were found between the readings in the two cases. For pressures above 60 atmospheres the second method was alone adopted. The astigmatism of the grating was purposely left uncorrected, because it was an advantage to have the extremities of the lines drawn out into points, as these indicated their most intense portions and enabled a more accurate setting of the cross-wires to be made. Two parallel threads in the eye-piece gave more consistent results than cross-wires.

As has already been stated, two sets of photographs, A and B, have been taken at pressures varying from 1 to 101 atmospheres (absolute).

Set A was measured first by the writer, and then by two assistants. Each observer obtained six readings of the displacement, making the total number of readings for each line 18. This number was frequently exceeded. For a second plate taken at the same pressure, 12 readings of each line were usually considered sufficient. The mean value of the shift of each line at each pressure was therefore obtained from at least 30 readings of the displacement. For Set A, 20,000 determinations of the displacements have been made.

Set B was measured by the writer alone, except in a few cases when separate observation seemed desirable, and the figures given in the table are the means of ten measurements of each displacement. The plates used for this set were Imperial Flashlight, and the Developer the Imperial Pyro-Metol Standard—a combination which was more successful than that previously used for Set A; the photographs were free from developer-fog, and the lines consequently measurable with much greater ease. The total number of readings for the second set is about one-third of the number made for the first set, but for the reasons given above, and also because experience is essential for the accurate determination of the positions of the most intense portions of the lines under pressure, the results given for the second set are considered more satisfactory.

The following photographs constitute the two sets :—

Set A.			Set B.	
Pressure in atmospheres.	Number of photographs.		Pressure in atmospheres.	Number of photographs.
	Pressure spectrum inside.	Pressure spectrum outside.		Pressure spectrum outside.
5	3	—	3	1
10	2	—	4	1
15	—	2	5	1
20	1	2	10	1
25	—	2	15	2
30	1	2	20	1
40	2	—	25	2
60	1	1	30	1
80	—	1	40	3
95	—	1	50	2
100	—	1	60	1
			70	1
			80	1
			100	1

Two photographs were usually taken upon each plate.
The first set are numbered D1 to D19.
The second set are numbered D21 to D33.

10. *Description of the Tables of the Displacements.*

The results of the measurements of the two sets of plates are given in Tables I. and II.

The first columns contain a list of arbitrary letters and numbers assigned to the different lines to facilitate reference to them. Beginning at the red end they run 1, 2, 3, 4, 5, 6, *a*0, *a*1, *a*2, *a*3. *a*4, *b*0, *b*1, *b*2, *b*3, *b*4, *c*0, *c*1, *c*2. &c. Plate 4 contains photographs showing lines beginning with 2 and ending with *j*0.

The second columns give the wave-lengths of the lines according to Kayser and Runge's tables.

In the subsequent columns the displacements of the lines at different pressures are set forth in thousandths of an Ångström unit. The use of black figures, *e.g.*, **223**, for displacements indicates that the line is reversed at the corresponding pressure, italic figures, *e.g.*, *223*, denoting a faint reversal; the displacements are those of the centre of the reversal. An asterisk * indicates that the line is reversed, but that the measurements of the displacements were not consistent. Numbers in brackets have not been plotted in the diagrams.

When two values for the displacement are given, one is for the line when reversed and the other for the unreversed line (measured on different plates). the upper number referring to the latter.

In all cases the shifts are towards the side of greater wave-length.

The pressures are the excess above one atmosphere.

Table I.—Set A.

Atmospheres . .		5.	10.	15.	20.	25.	30.	40.	60.	80.	95.	100.
Line.	Wave-length.	Displacements in thousandths of an Ångström unit.										
1	(4531·25)†	35	46	—	100	—	108	116	160	240	280	289
2	4528·78	47	*75*	128	*103*	*231*	215	270	259	421	404	452
3	4494·67	46	62	103	213	274	185	172	241	371	403	323
4	4482·35	44	51	78	193	298	121	177	237	393	388	345
5	4476·20	21	22	60	62	129	90	73	103	139	190	177
6	4466·70	24	27	34	*41*	*118*	78	69	95	175	177	181
(*a*)	4461·75	25	24	37	**48**	*	82	69	82	148	95	194
1	4459·24	43	64	71	211	254	203	177	263	362	365	431
2	4447·85	38	64	92	187	246	185	203	259	366	(315)	362
3	4443·30	26	25	57	94	105	86	78	129	160	—	134
4	4442·46	34	63	93	172	204	172	172	211	306	—	323
(*b*)	4430·74	37	63	66	155	207	172	172	293	—	(277)	323
1	4427·44	23	16	49	**28**	*	73	78	86	148	181	—
2	4422·67	25	22	75	68	107	69	65	112	195	185	134
3	**4415·27**	**30**	**22**	**47**	**52**	**103**	**82**	**73**	**138**	**222**	**250**	**(121)**
4	**4404·88**	**25**	**22**	**50**	**64**	**110**	**82**	**69**	**142**	**190**	**(224)**	**(138)**
(*c*)	**4383·70**	**26**	**19**	**53**	**78**	**103**	**65**	**82**	**138**	**198**	**194**	**(121)**
1	4376·04	22	21	27	**30**	*	73	73	95	129	82	—
2	4369·89	26	16	39	69	95	65	69	95	194	147	—
3	4352·86	39	16	31	51	108	69	60	82	147	164	—
4	4337·14	28	26	37	**93**	**185**	95	103	116	220	181	—
(*d*)	**4325·19**	**22**	**25**	**57**	**75**	**102**	**69**	*	**129**	**211**	**207**	**151**
1	4315·21	19	—	*28*	**42**	**86**	**69**	—	86	151	125	108
2	**4307·96**	**23**	*	**38**	**65**	**86**	**91**	*	**138**	**198**	**198**	**155**
3	4299·42	64	*133*	*209*	**126**	**224**	474	—	474	603	582	646
4	4294·26	33	**31**	**29**	**47**	**101**	**73**	**99**	116	164	263	172
(*e*)	4282·58	18	**15**	**30**	**35**	**90**	**56**	**59**	90	125	159	121
1	**4271·93**	**22**	**30**	**93**	**94**	**99**	**82**	**95**	**142**	**215**	**237**	**172**
2	4271·30	68	—	*	**75**	*	—	—	—	—	—	—
3	**4260·64**	**31**	**54**	**71**	**84**	**183**	**159**	**198**	*323*	754	862	991
4	**4250·93**	**18**	**30**	**33**	**55**	**97**	**78**	**82**	*116*	211	—	181
(*f*)	4250·28	—	(104	—	**83**	**172)**	—	—	—	—	—	—
1	4236·09	83	147	355	**122**	**211**	517 **155**	733	625	776	776	948
2	4233·76	86	133	239	534 **107**	**190**	431	474	453	491	(431)	603
3	4227·60	119	105	452	440 **122**	**195**	560	582	582	—	—	—
4	4222·32	75	81	241	440	—	388	409	431	—	—	—
(*g*)	4219·47	26	29	63	**56**	**105**	78	108	134	185	241	(125)
1	(4210·48)†	67	72	157	345	323	259	241	362	297	375	—
2	4204·07	23	16	56	(121)	—	90	95	129	—	—	134
3	**4202·15**	**13**	**17**	**41**	**38**	**101**	**69**	**90**	**121**	**198**	**211**	**188**
4	4199·19	23	**36**	**42**	**40**	**116**	**69**	**82**	*150*	224	134	134
5	4198·42	(96	103	—	**127)**	*	*	—	—	—	—	—
(*h*)	4191·57	81	122	263	530	—	345	431	496	(388)	(388)	733
1	4187·92	(66	120	349	**94**	**215)**	*	—	—	—	—	—
2	4187·17	76	123	213	**128**	*	*	—	—	—	—	—

Asterisks and black figures indicate reversals. Italic figures indicate faint reversals.

† See note on p. 138.

TABLE I.—Set A (continued).

Atmospheres . .		5.	10.	15.	20.	25.	30.	40.	60.	80.	95.	100.
Line.	Wave-length.	Displacements in thousandths of an Ångström unit.										
3	4181·85	25	30	**55**	**42**	**90**	**69**	**78**	116	181	228	207
4	4175·71	26	27	**47**	**68**	116	86	103	129	181	259	186
(*i*)	4156·88	23	21	**41**	**52**	*	73	99	129	164	172	172
1	4154·57	27	21	**58**	**41**	*110*	78	99	151	168	151	155
2	**4143·96**	**19**	**22**	**71**	**76**	**103**	**99**	**78**	**129**	**181**	**233**	**233**
3	4143·50	18	21	*	**48**	**69**	**39**	78	—	—	—	—
4	4134·77	19	20	62	**32**	**77**	103	112	125	194	177	185
(*j*)	**4132·15**	**16**	**24**	**45**	**59**	**92**	**86**	**95**	**129**	**259**	*	**289**
1	4127·68	20	25	*	**107**	**130**	**90**	95	108	172	168	215
2	4118·62	21	29	**56**	**70**	**110**	**95**	95	103	194	164	198
3	**4071·79**	**19**	**23**	**37**	**75**	**95**	**82**	**82**	**142**	**185**	**241**	**220**
4	**4063·63**	**20**	**25**	**40**	**67**	**86**	**73**	**95**	**138**	**198**	**250**	**233**
(*k*)	4062·51	17	25	—	**44**	*	—	—	—	—	—	—
1	**4045·90**	**20**	**25**	**25**	**77**	**107**	**73**	**103**	**147**	**185**	**250**	**267**
2	4033·16	26	37	—	**58**	*	—	—	—	—	—	—

TABLE II.—Set B.

Atmospheres . .		3.	4.	10.	15.	20.	25.	40.	50.	70.	80.	100.
Line.	Wave-length.	Displacements in thousandths of an Ångström unit.										
1	(4531·25)†	21	—	32	—	—	56	78	99	142	—	—
2	4528·78	—	—	*	86	**108**	138	172	177	259	284	340
3	4494·67	46	47	73	99	129	129	168	172	259	276	349
4	4482·35	—	45	—	86	—	86	—	151	237	259	306
5	4476·20	14	22	26	36	51	39	42	56	86	125	151
6	4466·70	16	—	26	43	40	44	46	56	86	125	147
(*a*)	4461·75	20	—	23	37	41	37	39	43	86	112	124
1	4459·24	46	47	79	95	116	121	172	185	254	289	345
1α	4454·50	—	—	22	—	—	—	—	—	—	142	—
2	4447·85	43	46	77	86	121	121	172	181	263	297	336
3	4443·30	17	24	28	47	47	43	60	73	103	116	164
4	4442·46	48	49	71	99	101	112	164	177	228	271	319
(*b*)	4430·74	41	—	71	103	108	108	159	194	276	284	340
1	4427·44	18	—	*23*	36	52	(22)	43	37	65	108	95
2	4422·67	18	—	28	47	44	43	46	52	78	112	138
3	**4415·27**	**24**	*	**41**	**46**	**52**	**62**	**78**	**112**	**121**	**172**	**228**
4	**4404·88**	**17**	**19**	**54**	**47**	*	**60**	**56**	**125**	**116**	**194**	**194**
(*c*)	**4383·70**	**16**	**20**	*	**56**	**62**	**62**	**60**	**142**	**116**	**198**	**198**
1	4376·04	18	—	*21*	31	**34**	37	47	36	56	86	138

Asterisks and black figures indicate reversals. Italic figures indicate faint reversals.

† See note on p. 138.

TABLE II.—Set B (continued).

Atmospheres . .		3.	4.	10.	15.	20.	25.	40.	50.	70.	80.	100.
Line.	Wave-length.	Displacements in thousandths of an Ångström unit.										
2	4369·89	**17**	—	33	32	40	43	60	60	108	129	134
3	4352·86	**21**	—	25	34	45	35	56	56	(47)	106	(106)
4	4337·14	30	31	42	62	69	66	82	73	121	185	194
(*d*)	**4325·19**	**18**	**21**	**32**	**56**	**62**	**65**	**56**	**125**	**112**	**203**	**185**
1	4315·21	15	24	*16*	31	**39**	37	41	43	56	108	99
2	**4307·96**	**16**	**20**	**24**	**56**	**60**	**56**	**60**	**112**	**95**	**194**	**177**
3	4299·42	—	—	**60**	155	*	207	313	—	470	474	560
4	4294·26	*	**21**	**24**	**47**	**52**	61	*86*	*142*	116	116	151
(*e*)	4282·58	*	**24**	**22**	*	**29**	33	56	*39*	—	116	95
1	**4271·93**	**14**	**23**	**21**	**45**	**64**	**65**	**69**	**129**	**147**	**203**	**203**
3	**4260·64**	**27**	**34**	**64**	**95**	**124**	**90**	**177**	**263**	**320**	*293*	732
4	**4250·93**	*	**18**	**22**	**46**	**58**	**56**	**82**	**116**	**129**	177	190
*f*1	4236·09	**31**	*	**64**	*95*	**129**	223	405	444	(776)	552	776
2	4233·76	99	92	193	172	297	203	370	409	465	483	668
3	4227·60	113	90	145	155	326	246	431	—	—	—	—
4	4222·32	86	71	140	177	265	196	358	—	543	517	—
(*g*)	4219·47	24	25	24	39	75	40	78	78	155	142	181
1	(4210·48)†	60	—	107	129	142	142	157	181	362	259	474
2	4204·07	21	—	22	30	—	43	60	61	134	121	190
3	**4202·15**	**21**	*	**21**	**47**	**49**	**60**	**78**	**116**	**116**	**190**	**228**
4	4199·19	*	*	**24**	**37**	**47**	**67**	**65**	**100**	**104**	121	181
5	4198·42	—	—	—	(147)	—	—	—	—	—	—	—
6	4196·31‡	(**174**	**210**	293	260)	—	—	—	—	—	—	—
7	4195·46‡	(**138**	**187**	284	250)	—	—	—	—	—	—	—
(*h*)	4191·57	—	—	188	190	271	183	310	—	443	452	539
1	4187·92	122	—	—	177	—	228	431	—	—	—	—
2	4187·17	106	—	—	177	321	(168)	(190)	—	—	—	—
2*a*	4184·99	—	—	24	—	—	—	47	94	—	—	172
3	4181·85	20	—	**25**	40	**43**	60	—	—	95	138	181
4	4175·71	24	—	21	49	60	52	65	47	108	142	172
(*i*)	4156·88	27	—	21	43	56	62	65	(39)	99	134	151
1	4154·57	24	—	22	46	54	57	86	(36)	112	129	172
2	**4143·96**	**14**	*	**26**	**56**	**60**	**70**	**99**	**138**	**155**	**181**	**177**
3	4143·50	18	—	*	30	**48**	—	—	—	—	—	—
4	4134·77	28	—	21	53	(142)	57	86	78	116	138	164
(*j*)	**4132·15**	**12**	*	**26**	**47**	**68**	**59**	**108**	**134**	**129**	*172*	*177*
1	4127·68	16	—	**41**	**47**	—	56	82	73	125	125	164
2	4118·62	26	—	**21**	41	71	59	99	86	142	125	177
3	**4071·79**	**20**	*	*	**59**	**60**	**69**	**86**	**129**	**147**	**181**	**198**
4	**4063·63**	**21**	*	*	**53**	**56**	**73**	**82**	**129**	**151**	**185**	**194**
*k*1	**4045·90**	**21**	*	*	**69**	**65**	**73**	**82**	**138**	**168**	*	*

Asterisks and black figures indicate reversals. Italic figures indicate faint reversals.

[† *Note added December*, 1907.—From a private communication from Professor KAYSER I understand that the lines 1, λ = 4531·25, and *g*1, λ = 4210·48, are the only ones in the above table that are doubtfully due to iron, being possibly produced by Co and Sa respectively. These lines alone fail to fall into any of the groups of lines into which the iron spectrum is divisible. There is thus additional evidence that they may be due to impurities. They have not been included in the diagrams.]

‡ See p. 157.

11. *Mean Values of Displacements.*

Table III.—Set A.

	Displacements in thousandths of an Ångström unit.										
Atmospheres	5.	10.	15.	20.	25.	30.	40.	60.	80.	95.	100.
Group I., unreversed	24	23	52	54	102	80	72	101	161	183	164
Group I., reversed	**21**	**23**	**45**	**67**	**101**	**74**	**86**	**136**	**203**	**227**	**191**
Group II.	41	63	94	194	245	187	185	252	371	359	366
Group III., unreversed	82	118	310	490	—	452	475	510	620	680	730
Group III., reversed	**31**	**54**	**71**	**109**	**203**	**157**	**193**	**323**	—	—	—

Table IV.—Set B.

	Displacements in thousandths of an Ångström unit.										
Atmospheres	3.	4.	10.	15.	20.	25.	40.	50.	70.	80.	100.
Group I., unreversed	20	23	27	43	52	45	62	59	102	122	153
Group I., reversed	**18**	**20**	**26**	**51**	**59**	**55**	**81**	**124**	**129**	**186**	**194**
Group II.	45	47	74	95	116	120	168	181	256	283	338
Group III., unreversed	100	84	166	171	280	212	374	426	539	510	655
Group III., reversed	**29**	**34**	**64**	**95**	**137**	**90**	**177**	**263**	**388**	**293**	*

12. *Discussion of the Displacement Tables and Curves.*

Tables I. and II., Diagrams I., II., III., and IV.

The values for the shifts given in Tables I. and II. have been plotted in Diagrams I. and II., in which the abscissæ represent the excess of pressure over one atmosphere, and the ordinates the increase in wave-lengths of the lines in thousandths of an Ångström unit.

Each line on the diagram depicts the behaviour under pressure of one spectral line, which may be identified by the letter attached to it. The reversal of a spectral line is indicated by the dotting of the line on the diagram near the pressure at which reversal takes place. Small arrows indicate those pressures at which measurements have been made.

The Curves and Tables show that—

(1) No lines remain undisplaced.

(2) The displacement is always towards the red end of the spectrum, indicating a decrease in the frequency of the vibrating particle.

(3) The displacement of the lines increases as the pressure is increased.

(4) The relation between the pressure and displacement is in general, but not quite rigorously, a continuous and linear one. (See pp. 145, 146.)

(5) The rates of increase of the displacement with the pressure vary greatly for different lines.

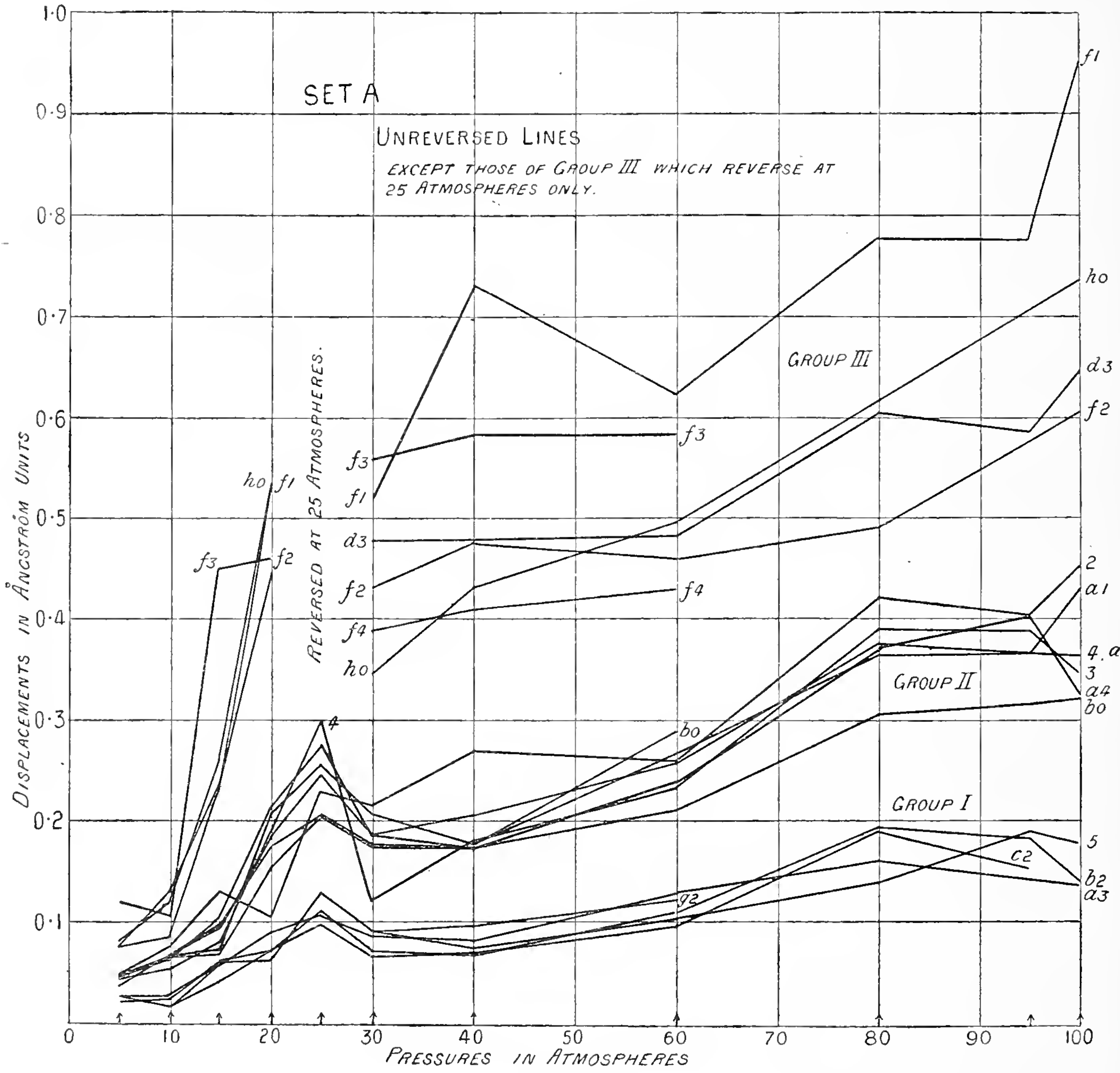


Diagram I.

No. 5 suggests a means for the classification of the lines: for example, the lines $f1$, $f2$, $h0$ always exhibit a much greater shift than do lines 2, 3, $a1$, whose displacements are themselves greater than those of the lines 5, 6, $a0$, &c. Three groups can in this way be definitely determined by the different values of the shifts of their several members.

In Group I. the lines are least shifted, and the wide range in the values of the shifts suggests that this group may be capable of resolution into simpler groups. The measurements of these lines were carefully repeated, but their diffuseness under pressure prevented great accuracy in the true setting of the lines, and all that could be definitely ascertained is that in both sets of photographs a few lines, *b*1, *c*1, *d*1, are less shifted than some others, for example the lines *c*4, *g*2, *h*3, *h*4, *j*1, *j*2. See Diagrams VII. and VIII., pp. 150 and 151, in which are plotted curves for the lines which reverse for a portion of the range of pressure.

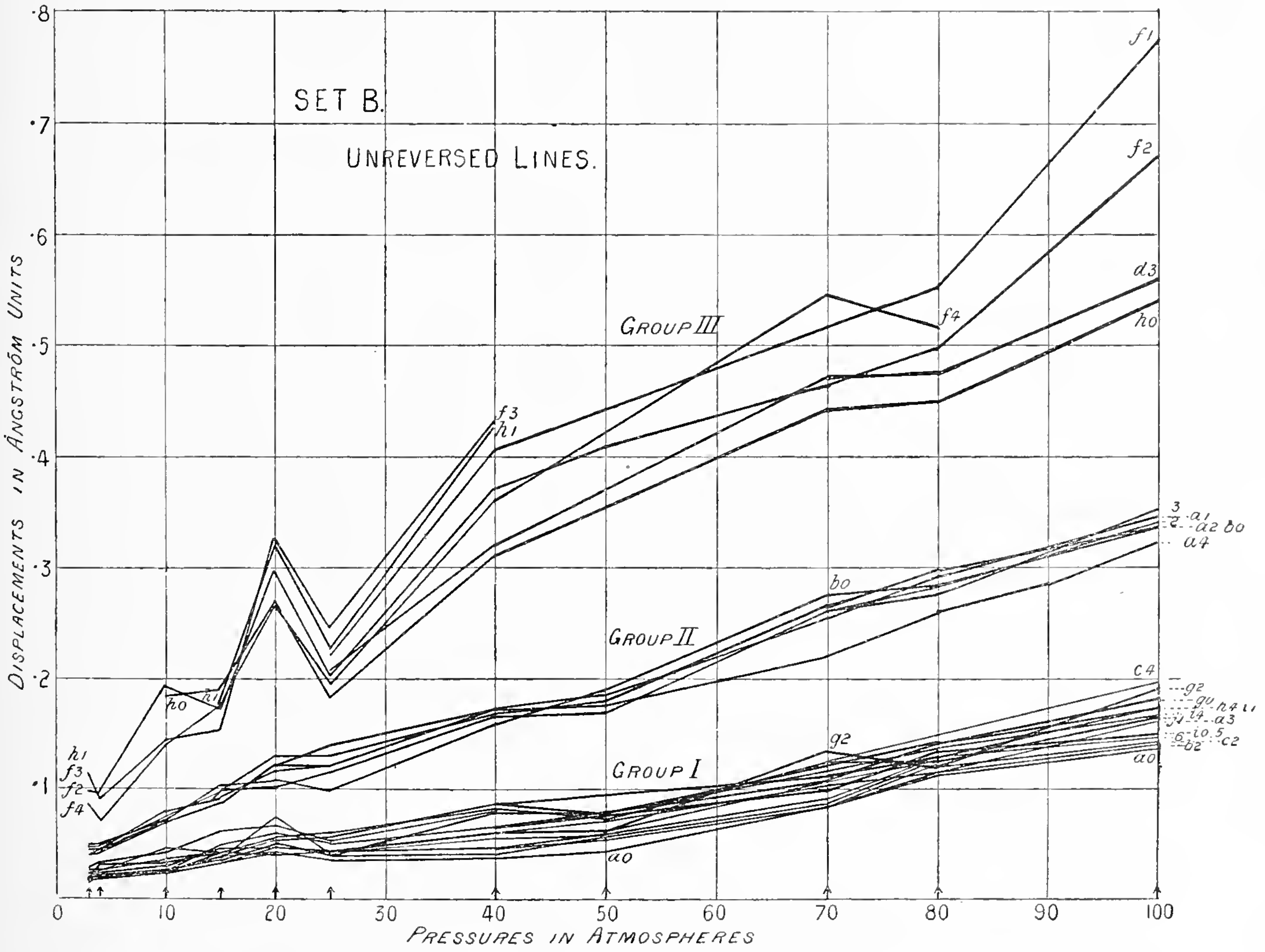


Diagram II.

The employment of poles not consisting entirely of iron, but of an alloy containing iron, or of an iron wire in a cored carbon, might facilitate the subdivision of this group, since it would decrease the widths of the lines and occasion greater accuracy in the measurements ; still it is not yet clear that the presence of another element is without effect upon the displacement of the lines. This is at present under investigation ; in the meantime it was considered advisable to avoid the use of an alloy.

The reversed lines of Group I. are plotted separately in Diagrams III. and IV.

Group II. contains fewer members and is more compact, all the lines showing remarkable agreement with one another. Diagrams I. and II. agree in assigning a low value to the shift of this line.

Line 4 also belongs to this group, but the presence of a faint line very close to it vitiated its measurements, which therefore have not been included in the diagram.

Group III. consists of lines which are invariably broad and diffuse under pressure, rendering their measurement a matter of great difficulty. As in the case of Group I., it is possible that two groups are united in Group III., but here again sub-division is not at present feasible, though there is some indication that the lowest members—the two lines *d*3 and *h*0—are to be treated apart from those exhibiting the greatest shift—*f*1, *f*2, *f*3, Diagram II. The difficulty of determining the true position of these lines is accentuated by the shape of their intensity curves, which under pressure are nearly flat-topped.

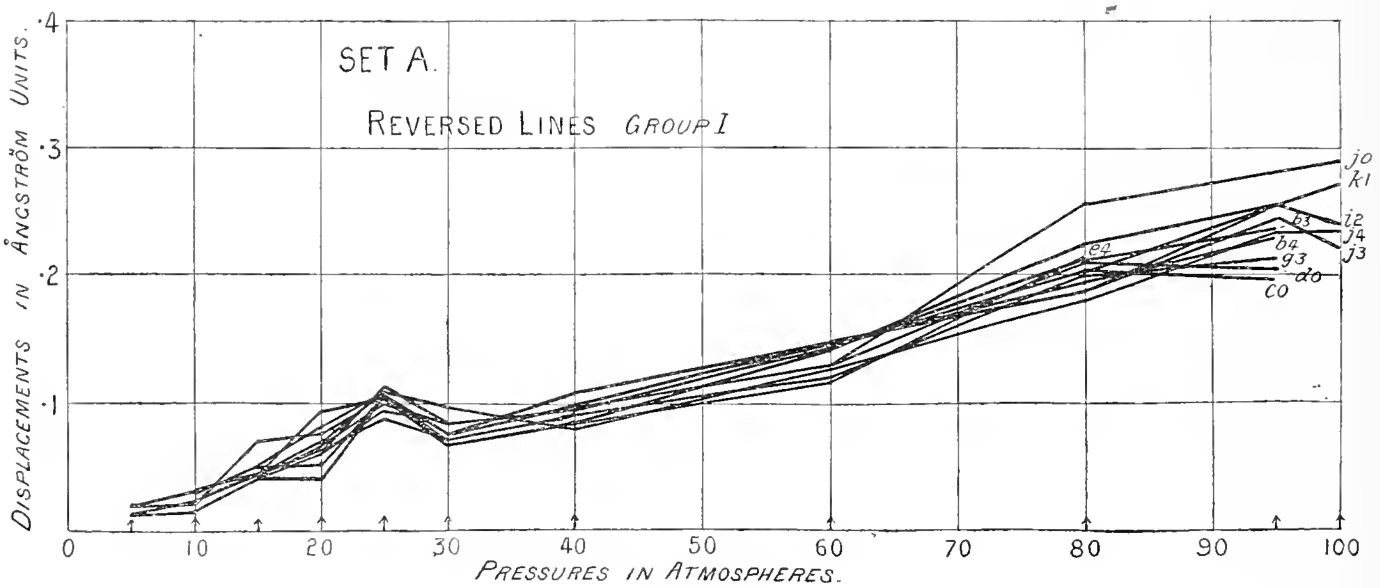


Diagram III.

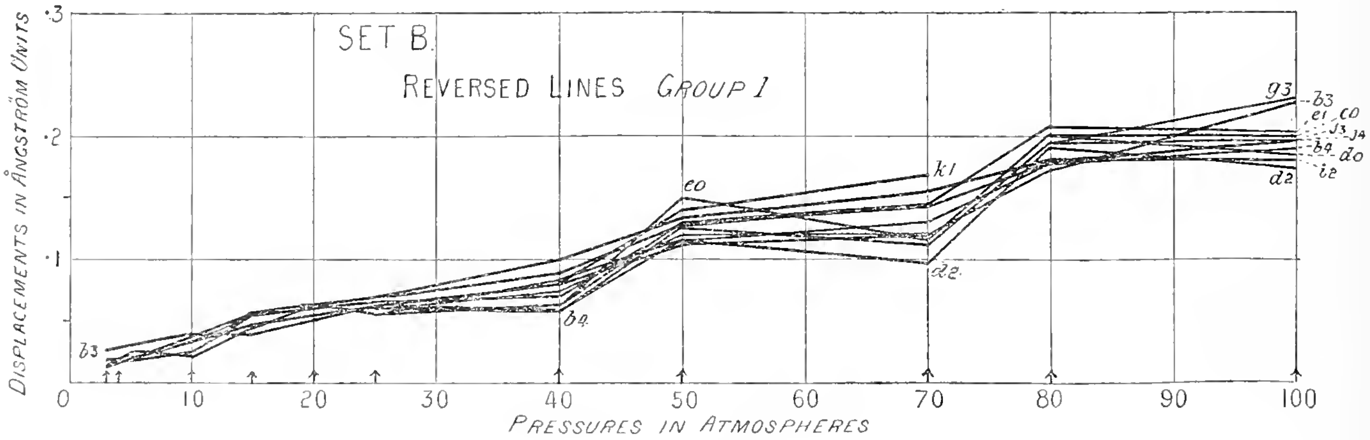


Diagram IV.

Group IV.—The existence ot a fourth group is suggested by the displacements of the lines *g*6, *g*7, but it is possible that their abnormal displacements are only apparent. (See p. 157.)

Tables III. and IV., Diagrams V. and VI.

The mean values of the displacements have been found for each group at each pressure, and the results for Set A are given in Table III., and those for Set B in Table IV.

For Groups I. and III. the reversed have been separated from the unreversed lines.

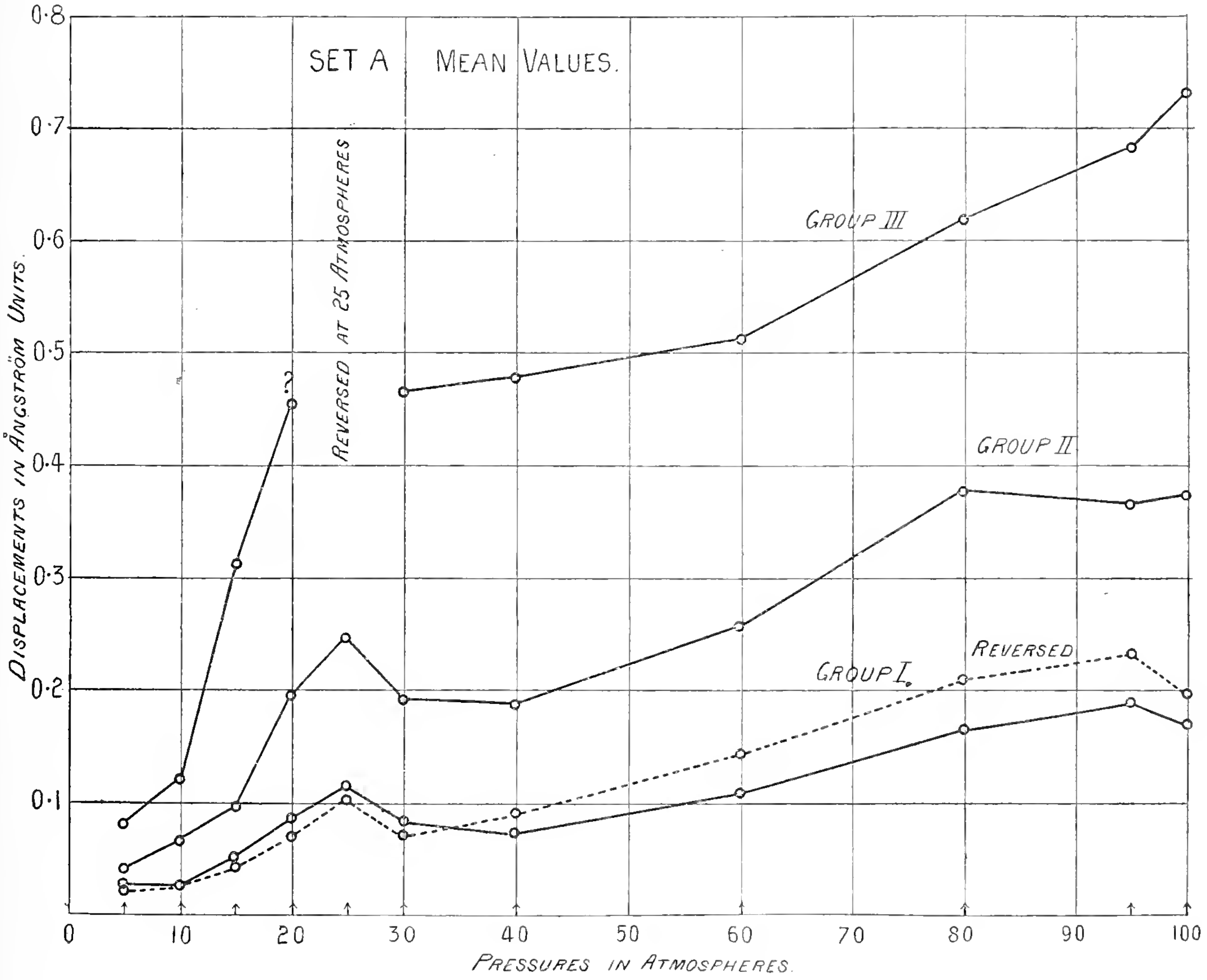


Diagram V.

Diagrams V. and VI. have been plotted from the Tables III. and IV. respectively, and refer both to reversed and unreversed lines. They emphasize the difference in magnitude of the displacements of the three groups, and exhibit graphically their rates of increase with pressure.

The increase of wave-length corresponding to a difference in pressure of 1 atmosphere, calculated on the assumption of a linear relation, is given below:—

	Thousandths of an Ångström unit.		Ratios.	
	Set A.	Set B.	Set A.	Set B.
Group I., unreversed . . .	1·9	1·5	1·0	1·0
Group II.	4·0	3·3	2·1	2·2
Group III., unreversed . . .	7·8	6·8	4·1	4·5

In the last two columns are given the ratios of the displacements of Groups II. and III. (unreversed lines) to that of Group I. (unreversed lines). The ratios are not very different from 1 : 2 : 4 for both sets, which, however, are not in this respect in accurate agreement, but this may perhaps be accounted for by some fogging of the plates of Set A, which renders the intensity curves rather too flat-topped and explains a tendency for the settings on the lines to be in them rather nearer the red end of the spectrum than in the photographs of Set B, in which the background is clear. On the side of the intensity curves on which the slope is gradual, the additional general exposure makes the percentage change in intensity less than it is

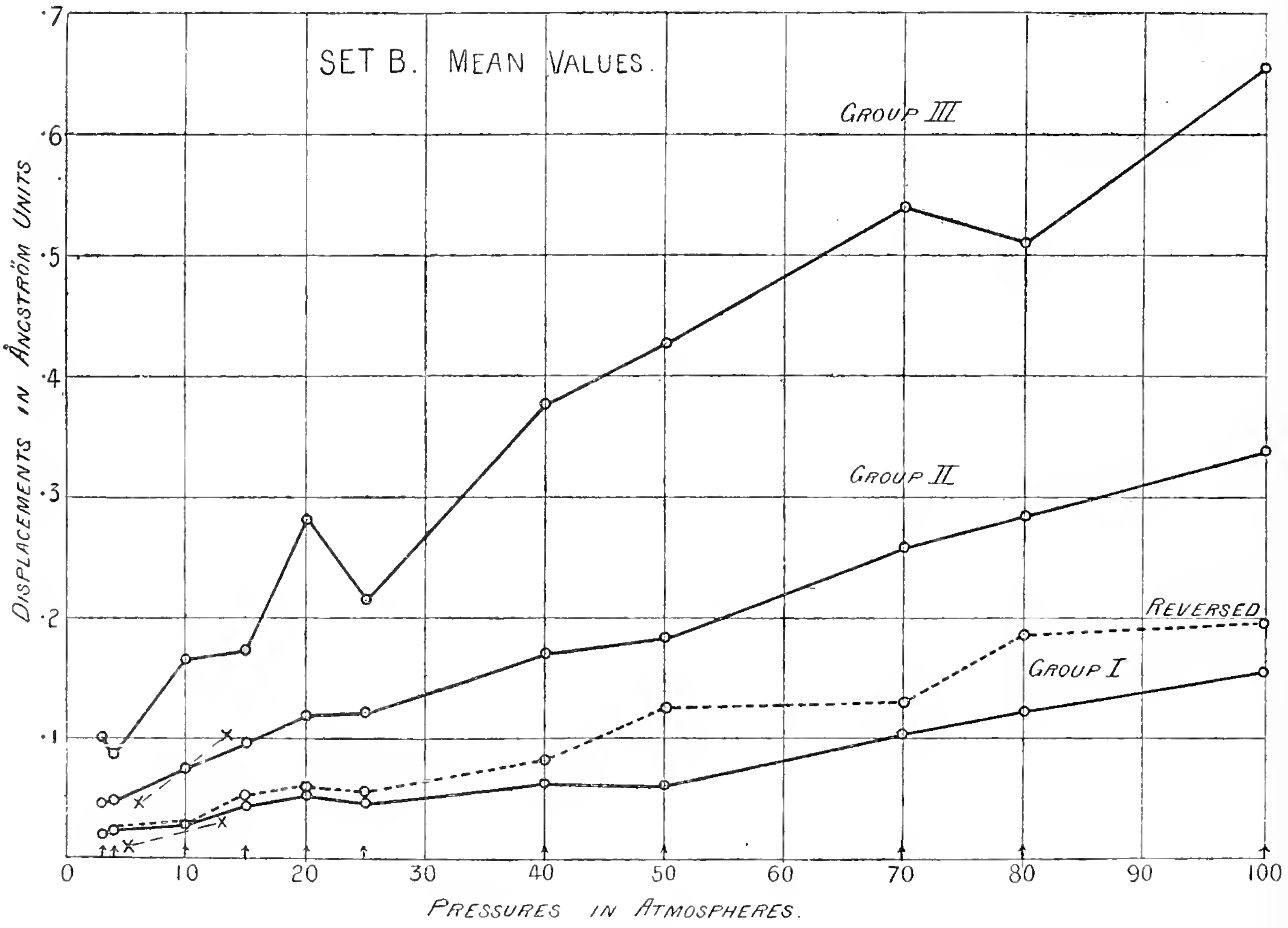
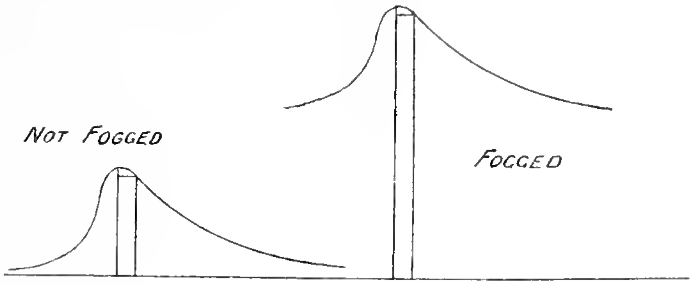


Diagram VI.

on the steeper side and less easily distinguishable by the eye. (See accompanying small diagram.)



The magnitude of this phenomenon is of an order which only interferes materially with the measurements of the lines of Group I.

Though roughly divisible into three groups, it is by no means certain that the shifts of all members are the same ; indeed, the converse is indicated by the displacement curves (Diagram II.), in which there is a tendency for the lines to maintain the same relative displacements throughout the range. The mean values of the shifts agree, however, to an extent which cannot be disregarded, in assigning to the ratios of the three groups the values 1 : 2 : 4, which HUMPHREYS states holds good for the spectra of other elements.

13. *The Relation between the Pressure and the Displacement.*

In August, 1906, the measurement of Set A was completed, but as the displacement curves then showed a departure from a linear relation between the displacement and the pressure at 15, 20, and 25 atmospheres (where the values were roughly double those required by the readings at other pressures for a linear connection to hold good, Diagrams I., III., V.), it was deemed advisable to re-measure the plates taken at those pressures. The second measurements agreed well with those originally obtained, but it was then found possible to measure a few of the strongest lines on another plate, D18, taken at 25 atmospheres, which had previously been rejected as being too under-exposed. The fourteen readings obtained from it indicated that the linear relation would be satisfied at that pressure if they were substituted for the readings given by photograph D19.

On both the photographs at 25 atmospheres the comparison spectrum was in the central strip, and as the precautions that had been taken (p. 129) seemed to preclude the possibility of an undiscovered fictitious shift, it was decided to investigate the phenomenon carefully, and to repeat the whole series of photographs.

The photographs of the second set, B, give results more consistent with a linear connection between the pressure and the displacement (Diagrams II., IV., VI.), except in the case of Group III., where the displacements at 20 atmospheres are again too high, though the readings given by Groups I. and II. agree well with those obtained at higher pressures in making the function a linear one.

At 5 atmospheres most of the lines of Groups I., Set A, as well as most of the lines of Set B, at 3 and 4 atmospheres, show too great a value for the linear relation to hold, and in this region the curves are not accurately directed to the origin; but too much stress must not be placed upon the measurements at these pressures, because the percentage error in the measurement of a shift is greater at low than at high pressures, since in the former the shift of the line is but a fraction of its own width. At higher pressures the percentage error is less, because the broadening of the lines does not increase as rapidly as their displacement.

The existence of the linear relation described by HUMPHREYS between the displacement and the wave-length is not confirmed by the present investigation. The discrepancies in the displacement of the lines of Groups I. and III. are not to be accounted for on this hypothesis, since the sequence of the lines on the diagram is not the same as their sequence on the photographs.

The conclusion arrived at from the displacement curves is that the relation between the pressure and the displacement is in general a linear one, but that it may be affected by a disturbing cause in the region 15 to 25 atmospheres.

14. *Phenomena relating to the Departure from a Linear Relation between the Pressure and Displacement.*

The photograph showing the most marked departure from the linear relation is D 19, taken at 25 atmospheres pressure, and its measurement by different observers is given in Table V., which also contains the readings obtained from three other plates, D18, D24, D25, taken at the same pressure. The last three agree well, and their mean values have been placed in the last columns of the table, where they may be compared with the mean values for Plate D19, given in the preceding column.

The table shows that the difference between the two plates is not to be explained by errors of measurement, and the fact that the discrepancy is different for different lines would in itself indicate that there had been no accidental disturbance of the camera, but we have additional evidence of this, because the two exposures of the comparison spectrum, which were taken before and after the pressure spectrum, are exactly superposed. An irregularity in the magnitude of the displacements might be introduced by the unlikely, but still possible, contingency of an alteration in the temperature, and therefore of the dispersive power, of the grating, during the exposure of the pressure spectrum, and a return to its original value for the second half of the divided exposure, but this irregularity would be progressive and should not displace the lines of one group more than those of another group when the members of the two are interspersed. There is strong evidence in favour of this phenomenon being a genuine one.

In the table the lines are arranged according to their groups, and the ratios of the shifts on Plate D19 to those on Plates D18, D24, and D25 for the different groups are as follows :—

TABLE V.

Plate . .	D19.		D18.	D25.		D24.		Mean values.		
								D19.	D18. D24. D25.	
Line.	Displacements in thousandths of an Ångström unit.									
		M.			M.		M.			
c3	164	203	—	90	93	87	—	183	90	Group III., reversed.
					Ratio			2·0	1	
f1	**211**	—	—	215	231	—	—	**211**	223	Group III., reversed and unreversed.
f2	**190**	—	—	185	220	—	—	**190**	202	
f3	**194**	—	—	237	—	—	—	**194**	237	
						Totals . .		**595**	662	
					Ratio			**0·9**	1	
3	267	280	159	121	142	157	155	274	146	Group II.
a1	271	237	142	103	129	—	—	254	125	
a2	263	226	—	86	129	103	142	246	116	
a4	—	204	—	95	112	101	116	204	103	
b0	233	181	—	91	99	97	—	207	95	
						Totals . .		1185	585	
					Ratio			2·0	1	
b3	**103**	**103**	**69**	**43**	**47**	—	—	**103**	**53**	Group I., reversed.
b4	**99**	**121**	**60**	**60**	**60**	—	—	**110**	**60**	
d0	**99**	**108**	**60**	**56**	—	—	—	**103**	**58**	
e1	**99**	**99**	—	**56**	—	—	—	**99**	**56**	
e4	**86**	**108**	—	**43**	—	—	—	**97**	**43**	
g3	**90**	**112**	—	**60**	**47**	—	—	**101**	**53**	
i2	**103**	—	—	**60**	**65**	—	—	**103**	**62**	
j0	**90**	**95**	—	**52**	**65**	—	—	**92**	**58**	
						Totals . .		**808**	**443**	
					Ratio			1·8	1	

The readings given in the columns marked M were made by assistants.
Numbers in black figures signify reversal.

Group I.	Reversed lines	1·8
Group II.	Unreversed lines	2·0
Group III.	Unreversed lines	1·8 ?
Group III.	Reversed lines	2·0

The ratio for the unreversed lines of Group I. is difficult to determine, since the readings of the plates made by different observers are not very concordant; it does not fall below 2.

The value for Group III. unreversed is derived from the readings for *f* 1, *f* 2, *f* 3, in which the value for D19 (reversed) is seen to be 0·9 times the mean value for the other three plates (unreversed). Section 16, p. 151, indicates that for this group the reversals are displaced roughly half as much as the emission lines, consequently, if unreversed lines in one case could be compared with unreversed lines in the other, the ratio of the displacements would be 1·8 to 1.

From Table VI. it may be seen that the photographs at 20 atmospheres exhibit the same phenomenon for Groups II. and III.; the values for the different lines are given in the Tables I. and II., and a comparison of them shows that the same kind of difference exists at this pressure as was found at 25 atmospheres.

At 15 atmospheres, also, discrepancies appear to exist between the values given by different plates for some of the lines, but at this pressure only the measurements for Group III. are discordant. There is a similar, but less marked, difference between the values for Group III. at 10 atmospheres; here it is the plate belonging to Set B that shows the higher values.

It has been suggested that the phenomenon may be due to different parts of the arc having been focussed upon the slit during the two exposures. Each photograph is, however, the integration of a number of short exposures due to the intermittent nature of the arc, and what is obtained on the photographic plate appears to be the average effect of the whole arc; nevertheless, the fact that reversals are found on all the plates shows that during each exposure we have been dealing with a hot central core surrounded by an absorbing envelope.

15. *The Displacement and the Tendency to Reverse.*

There is some evidence that the abnormal displacements measured in the region between 15 and 30 atmospheres are connected with the great tendency of the lines to reverse at these pressures. The Displacement Tables, I. and II., in which the lines which are reversed are distinguished from the rest, show that at 25 and 20 atmospheres, in Sets A and B respectively, the maximum number of reversals occurs, and the photographs also indicate that at these pressures the reversals are specially broad and strong. These are precisely the pressures at which the displacements in the two sets show their most marked departures from a linear relationship.

HALE and KENT* have remarked, for the spark discharge in compressed gases, that "when a bright line is beginning to show signs of reversal, or when bright and dark lines occur in pairs, the observed pressure shifts are irregular, probably because the overlapping lines prevent settings from being made on their true centres." The phenomenon is, however, in the present research presented by lines of Set A which are symmetrically reversed, and these should not be affected by overlapping. For unreversed lines belonging to Group III. (which reverses unsymmetrically) the existence of a faint absorption line on the edge of an emission line would imitate a very large displacement of the bright line, as HALE and KENT suggest, but these have been searched for carefully, and no displacements are included in this paper in which there is any suspicion of error due to such a disturbing cause. Plate 6, fig. 2, shows two lines, *f* 1 and *f* 2, belonging to Group III.; the former is reversed, but the latter presents no trace whatever of any absorption which might affect the accuracy of the readings. The evidence points to the phenomenon being due to pressure and not to errors of observation.

TABLE VI.

(The Displacements are in Thousandths of an Ångström Unit.)

Atmospheres.	Plates.	Number of reversals.	Mean values of displacements of Groups			Ratios of displacement, Group		
			I.	II.	III.	I.	II.	III.
25	D19$_a$	43	102	245	**203**	2·3	2	1 = 2†
	D18$_a$, 21$_b$, 22$_b$	15	45	120	212	1	1	1
20	D8$_a$, 9$_a$, 16$_a$	43	54	194	490	1	1·7	1·8
	D27$_b$	24	52	116	280	1	1	1
15	D19$_a$	26	52	94	310	1·2	1	1·8
	D24$_b$, 25$_b$	18	43	95	171	1	1	1
10	D31$_b$	26	27	74	166	1·2	1·2	1·4
	D4$_a$, 7$_a$	19	23	63	118	1	1	1

† See next section, p. 151.

The evidence that favours a connection between the tendency to reverse and the abnormal displacements is comprised in Table VI., in which the displacements of the lines shown by a photograph are compared with the number of reversals on that photograph. In those cases in which two or more photographs show the same number of reversals at the same pressure, the mean values of the displacements have been taken. The table shows that, in all cases in which there is a discrepancy

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* HALE and KENT, 'Publications of the Yerkes Observatory,' Vol. III., Pt. II., 1907.

between the values for the displacement, the photograph giving the higher value contains more reversed lines.

The ratios of the displacements are also given, and the higher value will be seen to be in each case (except at 10 atmospheres, where the accuracy is probably not as great as in the other cases) roughly twice the lower value.

Another peculiarity is that at 10 and 15 atmospheres pressure only Group III. is affected, that both Group II. and Group III. are affected at 20 atmospheres, and that at 25 atmospheres all the groups may show abnormal displacements. Whatever may be the nature of the disturbing cause, Group III. appears to be most susceptible to it.

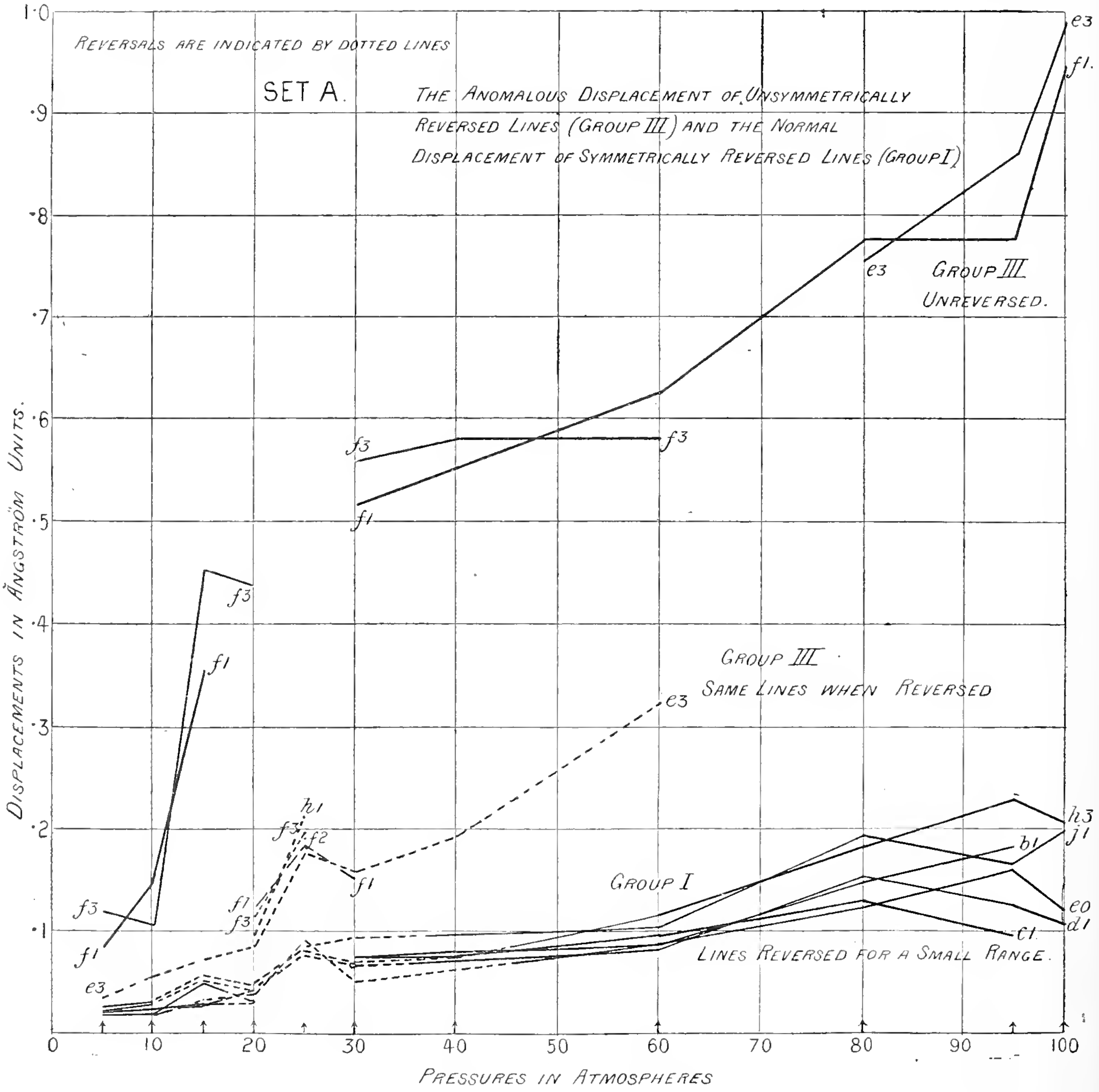

Diagram VII.

NOTE.—In this diagram the doubtful value for $f1$ at 40 atmospheres has been omitted.

16. *The Anomalous Displacement of Unsymmetrically Reversed Lines.*

Tables I. and II., pp. 136 and 137, show that several lines reverse for a small range of pressure only.

Diagram VII. illustrates the behaviour of lines of this type belonging to Set A, Groups I. and II., the dotted parts of the curve relating to the reversed line. It is apparent that for Group I. the atom absorbing the vibration follows the same course under pressure as the one producing the radiation. But this is not the case for the reversed lines of Group III., whose displacement curves may be compared with the displacement curves for unreversed lines belonging to this group, and also with their own displacement curves for that range of pressures during which reversal does not take place.

The remarkable fact is brought to light that the *lines of Group III. present two rates of increase of the displacement with pressure—one for the lines when unreversed, and the other, very much lower, for the line in its reversed state.*

Corroborative evidence of this phenomenon has been obtained from the second series of photographs, Set B, for which similar curves are shown in Diagram VIII.

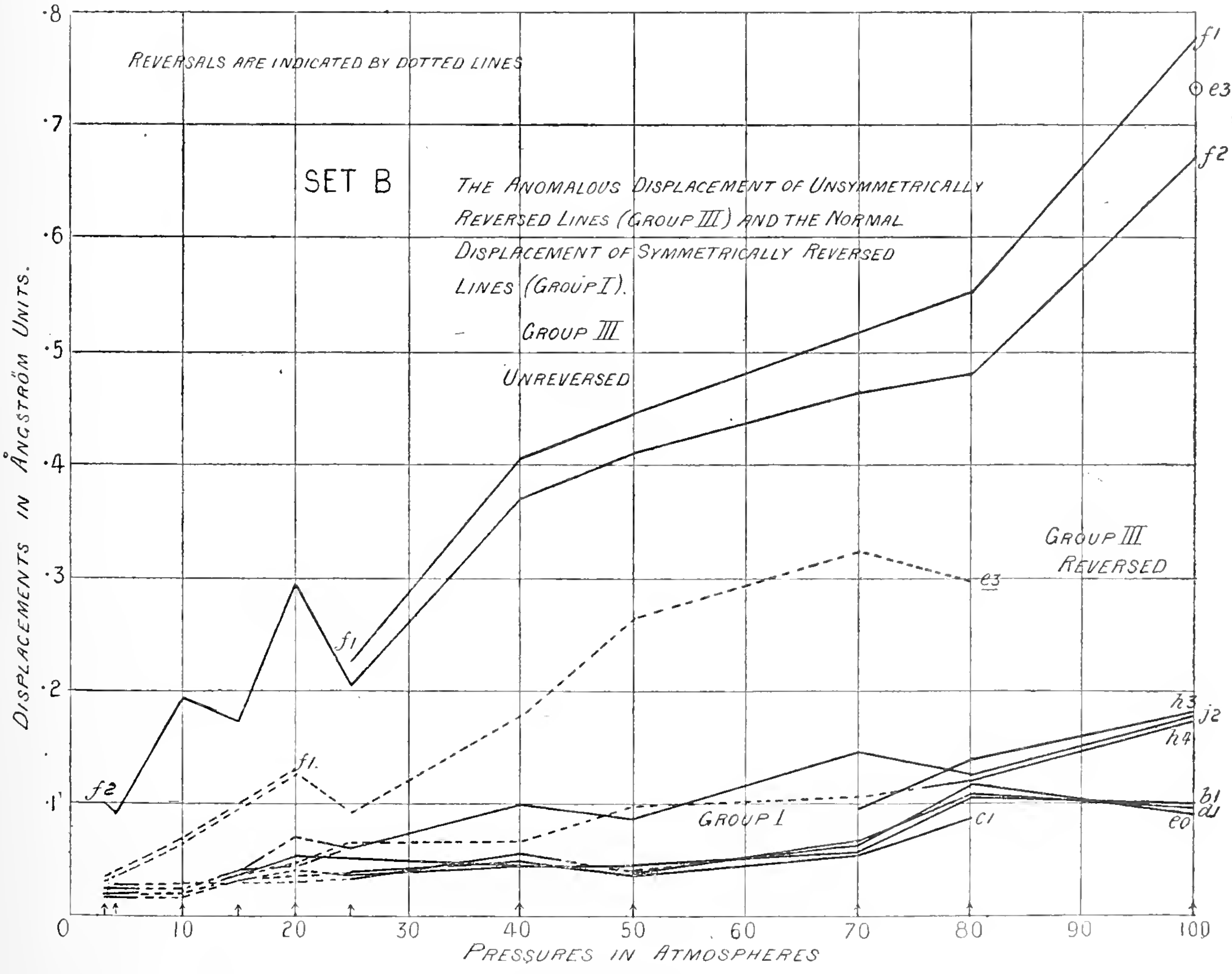

Diagram VIII.

These agree well with those obtained from Set A, and testify to the fact that the lines of Group III., when reversed, fall approximately in Group II.

The ratio of the displacements of the unreversed to those of the reversed lines of Group III. is for Set A 1·6, and for Set B 1·7, if the general directions of the curves be considered. From individual values at the pressures at which actual readings have been made, the ratio is very much higher, but the uncertain region, 15 to 30 atmospheres, has then an undue influence.

Diagram VIII. emphasizes the possibility of subdividing Group I.

17. *The Reversal of Lines under Pressure.*

It has already been pointed out (p. 133) that the immediate effect of pressure is to increase the number and intensity of the reversals, and that there is a pressure at which the reversals reach a maximum in these respects. The varying tendencies of the different lines towards reversal may be studied in the two tables of displacements, in which the number indicated by different type signifies that at the corresponding pressure the spectral line is reversed.

It will be seen that

Lines Originally Not Reversed either

(1) remain without reversal throughout the whole range of pressures investigated, *e.g.*, 3, 4, 5, *a*1, *a*3, *c*2, *c*3, &c.; or

(2) suffer reversal for a certain range of pressure, and then, as the pressure is increased, return to their initial condition. For Set A the range is 15 to 25 atmospheres. For Set B the greatest tendency to reverse occurs at 20 atmospheres. Lines belonging to this class are: *b*1, *c*1, *d*1, &c. (Diagram VIII.).

Two lines appear to suffer reversal in the neighbourhood of 3 to 5 atmospheres in Set B, and then to return to their unreversed condition. These lines are remarkable also for their large displacements under pressure. They are *g*6, *g*7, and are discussed under the heading of "Lines Enhanced under Pressure," p. 156.

Lines Originally Reversed

Continue as reversed lines up to the highest pressure. These are almost invariably strong lines, and their reversals are broad, *c*0, *d*0, *d*2, &c. The width, however, decreases in the neighbourhood of 100 atmospheres, and two of these lines in Set A do not show reversal above 80 atmospheres.

For Set A the reversals become more numerous and stronger up to 25 atmospheres, but at higher pressures they decrease in number and intensity. For Set B the maximum occurs at 20 atmospheres, though at 10 atmospheres they are also numerous, but not so broad. It may be that the paucity of reversals at the highest pressures is due entirely to the short duration of the arc in those regions, but though this undoubtedly causes a decrease in the amount of metallic vapour surrounding the arc, there must be a large number of atoms capable of absorbing certain vibrations even at 100 atmospheres, since at that pressure broad reversals are still apparent for the lines *c*0, *d*0, *d*2, &c.

It is interesting to note that it is at the pressure at which the maximum number of reversals occurs (20 to 25 atmospheres) that the change occurs in the amount of condensation upon the window of the pressure cylinder, mentioned on p. 131. This suggests that the size of the chamber possibly has some influence in determining the pressure at which the maximum number of reversals is found.

The reversals are of two types, (α) symmetrical, and (β) unsymmetrical. Examples of (α) are *b*3, *b*4, *c*0, *d*0, *d*2, Plate 4, and *e*1, *e*4, Plate 8. Example of (β) is *e*3, Plate 8.

In the measurement of all reversed lines the centre of the reversed portion has always been taken as its true position. For symmetrical lines this is probably strictly correct, and for the accuracy of the measurements it is fortunate that only lines of this type are found with broad reversals. It may not be accurate for type β, but any error introduced is not large, because the total width of a reversal is only a small percentage of the displacement associated with lines of this type.

It not infrequently happens that the same line occurs on two different plates taken at the same pressure with different amounts of reversal (see page 149). ANDERSON* has discussed the possible effect of the duration of the exposure on the widths of reversed lines, but the plates taken during the progress of this research were all sufficiently exposed for this cause to be negligible, and the determining factors are the amount and the temperature of the vapour in front of the arc, which are liable to variations on account of the fluctuations in the current which accrue from the continual striking of the arc, and from its comparatively short duration.

On this account the photographs show an integration of the effects of the temporary distributions of the vapour round the arc, and in view of this fact the labour of measuring the widths of the reversals has not been undertaken, especially as the widths are different on different plates at the same pressure, but inspection of the plates brings forward the fact that in general *those lines which reverse similarly are also displaced by equal amounts under pressure.* For example, the lines *b*4, *d*0, *d*2, *e*1 are reversed symmetrically and have approximately the same widths of reversal, and their wings are of the same nature; it will be seen, too, that their displacement curves also agree. Lines *b*1, *c*1, *d*1, *e*0 also reverse similarly and equally, and they are displaced to the same extent (Diagram VIII., p. 151). The converse is not necessarily true.

The reversals show no tendency to undergo change of type as the pressure is increased; those lines that at low pressures are unsymmetrically reversed are, if reversed at all at higher pressures, still of type β. Those of type α preserve their

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* ANDERSON, 'Astrophysical Journal,' XXIV., 238, 1906.

approximate symmetry. The photographs also show that *in all cases of unsymmetrical reversal occurring between* 4000 *and* 4500 *Å.U., the absorbed part of the line is on the violet side of the emission line.*

(This phenomenon occurring in the arc has been observed in spark discharges in liquids and gases under pressure by HALE and KENT,* and by ANDERSON.† WILSING,‡ LOCKYER, § and HALE and KENT* have discussed its bearing upon the spectra of New Type Stars.)

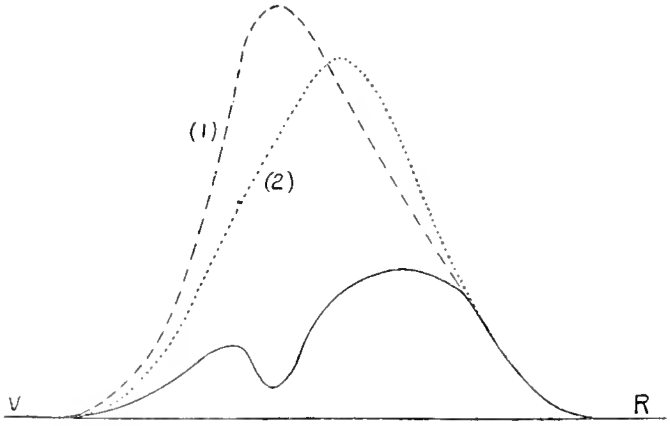

Fig. 11.

For unsymmetrically reversed lines under pressure the intensity curve is of the nature shown by the full line, fig. 11, which may be due either to the emission line represented by the dotted curve (1) (in which the maximum ordinate coincides with the centre of the absorption line) or that represented by the dotted curve (2) (in which it is on the red side of it), together with corresponding amounts of absorption.

The present experiments afford a means for deciding upon the correct emission line, because it is not unusual to find that some lines are reversed on one photograph at a definite pressure, but not on another taken at the same pressure :—

e.g., at 15 atmospheres line *f*1 is reversed on plate D25, but not on D19,
,, 20 ,, ,, *f*2 ,, ,, D9, D16, ,, ,, D27,
,, 30 ,, ,, *f*1 ,, ,, D9, ,, ,, D26,
,, 80 ,, ,, *e*3 ,, ,, D32, ,, ,, D15.

The position of the most intense portion of the bright line has been determined from one plate, and in all cases its displacement towards the red has been found to be greater than that of the absorption line on the other plate, Table VII. Hence the maximum of the intensity curve for the emitting atom falls in such cases of unsymmetrical reversal on the red side of the absorption line on the photographic plate, *i.e.*, the curve (2) more nearly represents the true emission line, and hence *in an iron arc, for the*

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* HALE and KENT, 'Astrophysical Journal,' XVII., 154, 1903.

† ANDERSON, 'Astrophysical Journal,' XXIV., 238, 1906.

‡ WILSING, 'Astrophysical Journal,' X., 113, 1899.

§ LOCKYER, 'Astrophysical Journal,' XV., 190, 1902.

unsymmetrically reversed lines of Group III., it is not in general the most intense portion of the emitted light that is absorbed.

This result might have been deduced from the displacement curves given in Diagrams VII. and VIII., which show that when the members of Group III. reverse, their reversals are at that pressure less displaced towards the red than are the emission lines.

Since the values of the displacements of *e*3 at 80 and 100 atmospheres correspond to those for the other lines of Group III., it is legitimate to assume that if its emission could be examined without the superposed absorption, its displacement curve would be identical with those of *f*1, *f*2, &c. This being the case, it is clear that its absorption line is on the violet side of the most intense part of the emission line, and it again follows that for the lines of Group III. the most intense vibration emitted is not necessarily that which is most strongly absorbed by the vapour surrounding the arc.

Only one line of Group II. shows reversal, and that is line 2, which reverses unsymmetrically at 10, 20, and at 25 atmospheres; its displacements at these pressures seem consistent with the absorption of its most intense emission, differing in this respect from the lines of Group III.

TABLE VII.

Pressure in atmospheres.	Line.	Wave-length.	Displacements in thousandths of an Ångström unit.	
			Reversed.	Not reversed.
15	*f*1	4236·09	95	355
20	*f*2	4233·76	108	296
30	*f*1	4236·09	155	344
80	*e*3	4250·64	293	754

From Table VII. the change in the frequency under pressure of the absorbing particles is less than one-half the change in the frequency of the primary radiation from the core of the arc, but as the measurements are taken from the region of anomalous displacements, and are from plates bearing different amounts of absorption, the readings are not strictly comparable; the better method is to derive the values from Diagrams VII. and VIII., when the displacements of the reversal approximate closely to one-half that of the emission line.

The suggestion that a possible cause of the anomalous displacements of the absorption lines is some interaction in the outer envelopes of the arc between the iron and the surrounding atmosphere of air is capable of experimental investigation by a study of the effect of different gases upon the spectrum, and this is on the programme for future work; but the effect of any such interaction would be the loading of the absorbing metallic systems, and the consequent increase in the wave-length of the light they absorb, whereas the opposite effect has been observed by ANDERSON,[*] who measured the displacements of some spark lines under pressure in atmospheres of carbon dioxide and hydrogen, and obtained larger values when the denser gas was used, but it is possible that the effect may be less obvious in the arc than in the spark, since in the former the surrounding gas will not presumably influence so strongly the nature of the discharge.

Differences in physical properties (density, temperature, specific inductive capacity, &c.) between the absorbing layer and the core of the arc, as well as the possible influence of abnormal dispersive properties of the surrounding vapours, have also been suggested as causes of this phenomenon. There is also considerable evidence in favour of the existence in the gaseous envelopes of a modified system derived from the iron atom.

18. *The Order of Reversal.*

In their study of the spectrum obtained from a spark discharge in liquids and gases under pressure, HALE and KENT[†] noticed that the reversals appeared first at the violet end of the region observed, 3550 to 4500 Å.U., becoming more intense and gradually extending towards the red end as the pressure about the spark was increased.

In the case of the arc spectrum of iron within the range of wave-lengths 4000 to 4500 Å.U., this phenomenon does not make its appearance between pressures of 1 and 101 atmospheres (absolute), the intensities of the reversals at the more refrangible end of the plate bearing very nearly the same ratio to the intensities of the reversals at the red end for all pressures.

A recent research[‡] affords a possible explanation of the difference between the results obtained by HALE and the present writer on the hypothesis that different temperature and radiation gradients exist in the arc and spark. These are shown to be determining factors in the reversals of lines when the same amounts of vapour are present—the steep gradient of the electric spark being more favourable than that of the arc for the production of this phenomenon.

19. *Lines Enhanced and Weakened under Pressure.*

The majority of lines continue throughout the range of pressure with nearly the same relative intensities that they possess at 1 atmosphere, but a few undergo a change and are enhanced as the pressure is increased, while others appear as weakened lines under high pressures.

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[*] ANDERSON, 'Astrophysical Journal,' XXIV., 221, 1906.

[†] HALE and KENT, 'Astrophysical Journal,' XVII., 154, 1903; also HALE, 'Astrophysical Journal,' XV., 227.

[‡] A. SCHUSTER, "Radiation through a Foggy Atmosphere," 'Astrophysical Journal,' XXI., 1, 1905

Attention was drawn to this phenomenon by what was at first thought to be the displacement of a line (*a*2) towards the violet. Under pressure this line appeared to have a reversal on the violet side of the comparison line, but the phenomenon has now been traced to the enhancing of a very faint line occurring close to *a*2 on its more refrangible side, which gave to the space between them the appearance of a reversal. It was also found that the only other apparent displacement of a line (*b*0) to the violet was due to a similar cause.

(The measurements given for two other lines are possibly vitiated by the appearance in close proximity to them, in this case on their red side, of two enhanced lines. The displacements tabulated for *g*6 and *g*7 are larger than those for any other lines at the same pressures [Table II.], and the range of pressures at which they are reversed, 3–5 atmospheres, does not coincide with the region of reversal for other lines. Their behaviour may possibly be explained by the enhancing of two faint lines on their red side. This consideration has prevented them from being definitely assigned to a Group IV. possessing a displacement about four times as large as that of Group II.)

An examination of Photograph 1, Plate 5, led to the discovery of several lines that are enhanced under pressure. The spectra were photographed under 1, +25, +50, +75, +100 atmospheres, and although the spectrum at 1 atmosphere is not exposed as much as the others, the relative intensities of the lines in it can be readily compared with their relative intensities in the other spectra. Pairs of lines to be compared are marked on the plate, and the member with the × will be seen to have increased in intensity under pressure. A list of such lines occurring in the region 4000–4500 Å.U. is given in Table VIII.

TABLE VIII.

Letter.	Wave-length.	
	LINES ENHANCED UNDER PRESSURE.	
*a*1*α**	4454·50*	
*a*3	4443·30	* Marked × on Plate 5, fig. 1.
*b*0	4430·74	
*b*2*	4422·67*	All enhanced lines are marked E on the same Plate.
*c*2*	4369·89*	
*g*0	4219·47	
	LINES WEAKENED UNDER PRESSURE.	
	4484·36†	† The weakening effect may be to some extent due to widening of the lines.
	4469·53†	
*e*2	4282·58	Weakened lines are marked W on Plate 5, fig. 1, and on Plate 8.
*f*0	4250·28	
	4247·60	
	4238·95‡	‡ Marked ○ on Plate 5, fig. 1.

NOTE.—The relative intensities also seem to vary in the different photographs at normal atmospheric pressure, but different amounts of exposure possibly account for this.

Above 25 atmospheres there is little change in the relative intensities, though the increasing width of some lines and their diffuseness make them appear weaker.

The line 4238·95 that has diminished in intensity under pressure is marked by an ○ on Plate 5, fig. 1, and it will be seen only in the spectrum under 1 atmosphere—at 25 atmospheres it seems to have been obliterated. The spectrum taken at a pressure of 1 atmosphere is under-exposed, so the difference in relative intensity is greater than is apparent on the plate. The other lines that are weakened are marked W on Plate 5, fig. 1, and on Plate 8. The two lines *f*0 and *e*2 do not appear to contribute anything to the wings of the symmetrically reversed lines *e*1 and *e*4.

A third class of phenomena relating to changes in intensity is exhibited by the line which occurs in the spectrum under 20 atmospheres, Set A, as a strongly reversed line, whose corresponding emission line in the comparison spectrum cannot with any certainty be ascertained* (see Plate 6, fig. 3).

The wave-lengths assigned to the enhanced lines are taken from KAYSER and RUNGE's tables. If any of them are due to impurities, the same impurity must have existed in the poles used by both KAYSER and RUNGE and the writer.†

20. *Series of Lines in the Iron Spectrum.*

From the displacement curves we have overwhelming evidence of the existence in the iron spectrum of lines of different types, see Section 12, p. 139. The photograph reproduced in Plate 5, fig. 2, in which the lines belonging to Groups I., II., and III. are linked together, shows that the lines possessing the same shift have in general the same appearance, and that their broadening and manner of reversal are similar.

The lines of Group I., which are characterised by their strong reversals, are linked by a dotted line and are marked Group I.R. The unreversed lines of Group I. are marked Group I.U.

The photograph only includes a portion of the region of the spectrum examined.

TABLE IX.

		Group I.	Group II.	Group III.
Displacement per atmosphere in Ångström units	Set A.	0·0019	0·0040	0·0078
	,, B.	0·0015	0·0033	0·0068
Ratio of shift	,, A.	1	2·1	4·1
	,, B.	1	2·2	4·5
Broadening under pressure		Rather broadened	Much broadened	Very broad and diffuse.
Type of broadening.		Nearly symmetrical	Unsymmetrical	Very unsymmetrical, almost a band.
Nature of reversals		Symmetrical	Unsymmetrical ?	Very unsymmetrical.

[* *Note added December* 1907.—Mr. H. F. NEWALL suggests that this may be due to the calcium line 4227 produced by an impurity which has found its way into the outer layers of the arc. This explanation must, I think, be accepted.]

† See note p. 138.

Table IX. shows the characteristics of the different groups, and indicates that they may be the Principal, First and Second Subordinate Series into which the spectra of other elements are generally divisible.

HUMPHREYS found that the ratios of the shifts for these series are for other elements 1 : 2 : 4, and that in the iron spectrum two groups exist with shifts in the ratio of 1 : 3.

As already suggested, the groups seem capable of further subdivision; for instance, *c*1 and *d*1 present differences in shift and in reversal from the majority of lines in Group I., Diagram VIII., p. 151. There are also very obvious triplets in the spectrum, as well as what are at present thought to be doublets. A detailed account of these is reserved for future publication, when a larger range of the spectrum has been investigated.*

The photograph, Plate 5, fig. 2, shows the remarkable "gregarious" tendency of the lines of Groups II. and III. The members of the former all occur at the less refrangible end of the region investigated, and those of the latter within a small range of wave-lengths near the centre.

HUMPHREYS states that the lines belonging to any group behave similarly when the source is placed in a magnetic field, but the Zeeman effect upon the lines investigated in the present research is not to hand.

The two groups into which HUMPHREYS originally divided the lines of the iron spectrum are shown by the broken lines XX in Diagram VI. As already stated, HUMPHREYS† has recently obtained a photograph at 37 atmospheres pressure; though the displacements given by it are of the same order as those obtained in the present research, the agreement between the readings is not as good as one would wish to find.

The evidence for the existence of a Group IV. has already been given (see Table II., p. 138, lines *g*6 and *g*7, also p. 157). The displacements are roughly eight times those of lines belonging to Group I.

In the present research the two sets of photographs agree in assigning the same lines to the same groups. A list of the lines belonging to each group is given in Table X., p. 160.

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* Attention may be drawn to the three lines *d*0, *d*2, *e*1 (λ for *d*2 = 4308), which appear to form a triplet in which the frequency relation between its members is approximately the same as that for the triplets *b*3, *b*4, *c*0 at 4404, and for *j*3, *j*4, *k*1 at 4063, though the frequency differences are not the same.

[† *Note added December*, 1907.—Subsequent to the presentation of this paper, a paper by HUMPHREYS has appeared in the 'Astrophysical Journal,' XXVI., 18, 1907, describing experiments in which photographs of arc spectra were obtained under pressures of 42, 69, and 101 atmospheres.]

TABLE X.

Line.	Wave-length.	Line.	Wave-length.
GROUP I.—UNREVERSED.			
5	4476·20	*g*0	4219·47*
6	4466·70*	*g*2	4204·07
*a*0	4461·75*	*g*4	4199·19*†
*a*1*α*	4454·50	*h*2*α*	4184·99
*a*3	4443·30	*h*3	4181·85*†
*b*1	4427·44*†	*h*4	4175·71*
*b*2	4422·67	*i*0	4156·88*
*c*1	4376·04*†	*i*1	4154·57*
*c*2	4369·89	*i*3	4143·50*†
*c*3	4352·86	*i*4	4134·77*
*c*4	4337·14*	*j*1	4127·68*
*d*1	4315·21*†	*j*2	4118·62*†
*d*4	4294·26*†	*k*0	4062·51*
*e*0	4282·58*†	*k*2	4033·16*
GROUP I.—REVERSED.			
*b*3	4415·27	*g*3	4202·15
*b*4	4404·88	*i*2	4143·96
*c*0	4383·70	*j*0	4132·15
*d*0	4325·92	*j*3	4071·79
*d*2	4307·96	*j*4	4063·63
*e*1	4271·93	*k*1	4045·90
*e*4	4250·93	—	—
GROUP II.			
2	4528·78*†	*a*2	4447·85
3	4494·67	*a*4	4442·46
4	4482·35	*b*0	4430·74
*a*1	4459·24	—	—
GROUP III.—UNREVERSED.			
*d*3	4299·42*†	*f*4	4222·32
*f*0	4250·28*	*g*5	4198·42*
*f*1	4236·09*†	*h*0	4191·57
*f*2	4233·76*	*h*1	4187·92*
*f*3	4227·60*	*h*2	4187·17*
GROUP III.—REVERSED.			
*e*3	4260·64	—	—
GROUP IV.‡ ?			
*g*6	4196·31†	*g*7	4195·46†

* Signifies that under pressure the line is reversed in Set A.

† „ „ „ „ „ Set B.

‡ *Cf.* p. 159.

21. *Summary of Results.*

The spectrum of the iron arc in air has been examined in the region λ = 4000 to λ = 4500, under pressures varying from 1 to 101 atmospheres (absolute).

I. *Broadening*:—

1. With increase of pressure all lines become broader.

2. The amount of broadening is different for different lines, some almost becoming bands at high pressures and others remaining comparatively sharp.

3. The broadening may be symmetrical or unsymmetrical; in the latter case the broadening is greater on the red side.

II. *Displacement*:—

1. Under pressure the most intense portion of every line is displaced from the position it occupies at a pressure of 1 atmosphere.

2. Reversed as well as bright lines are displaced.

3. With increase of pressure the displacement is towards the red side of the spectrum.

4. The displacement is real and is not due to unsymmetrical broadening.

5. The displacements are different for different lines.

6. The lines of the iron arc can be grouped into series according to the amounts of their displacements.

7. Three groups can in this way be distinguished from one another; the displacements of Groups I., II., III. bear to one another the approximate ratio 1 : 2 : 4. (The existence of a fourth group is suggested by the behaviour of two lines, but further evidence is needed upon this point. 1 : 2 : 4 : 8 would be the relations existing between the four groups.)

8. Though all the lines, with two exceptions, fall definitely into one or other of these groups, the lines belonging to any one group differ to an appreciable extent amongst themselves in the amounts of their displacements.

9. The relation between the pressure and the displacement is, in general, a linear one, but some photographs taken at 15, 20, and 25 atmospheres pressure give readings incompatible with this relation. Other photographs at 15 and 25 atmospheres present values which are compatible with it.

10. The abnormal readings are approximately twice those required by the displacements at other pressures for the displacement to be a continuous and linear function of the pressure.

11. On the photographs showing abnormal displacements, the reversals are more numerous and broader than they are on plates giving normal values, and there is some evidence in favour of a connection between the occurrence of abnormal displacements and the tendency of the lines to reverse.

III. *Reversal*:—

1. As the pressure is increased, reversals at first become more numerous and broader.

2. The tendency to reverse reaches a maximum in the neighbourhood of 20 to 25 atmospheres, and a further increase in pressure reduces their number and width.

3. Two types of reversal appear on the photographs, symmetrical and unsymmetrical.

4. Within the range of pressures investigated, the reversals show no tendency to change their type.

5. In the case of unsymmetrically reversed lines in the electric arc, the reversed portion does not in general correspond to the most intense part of the emission line, being usually on its more refrangible side.

6. The displacements of the reversed parts of the unsymmetrically reversed lines of Group III. are about one-half the displacements of the corresponding emission lines. Indeed, the reversed parts of the lines of Group III. fall approximately in Group II.

7. No relation between the order of reversal and the frequency of vibration, such as exists in the spark, has been observed in the iron arc for the ranges of wave-length and pressure examined.

IV. *Intensity*:—

1. The intensity of the light emitted by the iron arc is, under high pressures, much greater than at normal atmospheric pressure.

2. Changes in the relative intensity of the lines are produced by pressure. Lists of enhanced and weakened lines are given.

I express with pleasure my appreciation of their services to Mr. T. Royds, B.Sc., who assisted me in the preliminary operations, and in taking and measuring the first set of photographs, and to Messrs. Bleakley, Riley, Rossi, and West, who assisted in the measurement of the plates and in the taking of the second set of photographs.

My indebtedness to Mr. Petavel, F.R.S., who designed the essential part of the pressure apparatus, has already been recorded.

The research was suggested to me by Professor Schuster, F.R.S., and for placing the necessary apparatus at my disposal and for his advice and inspiring interest I am very grateful.

In conclusion, I cannot resist the opportunity of expressing my admiration of the work of Humphreys and Mohler, the pioneers in this subject, whose results are here, in the main, confirmed.

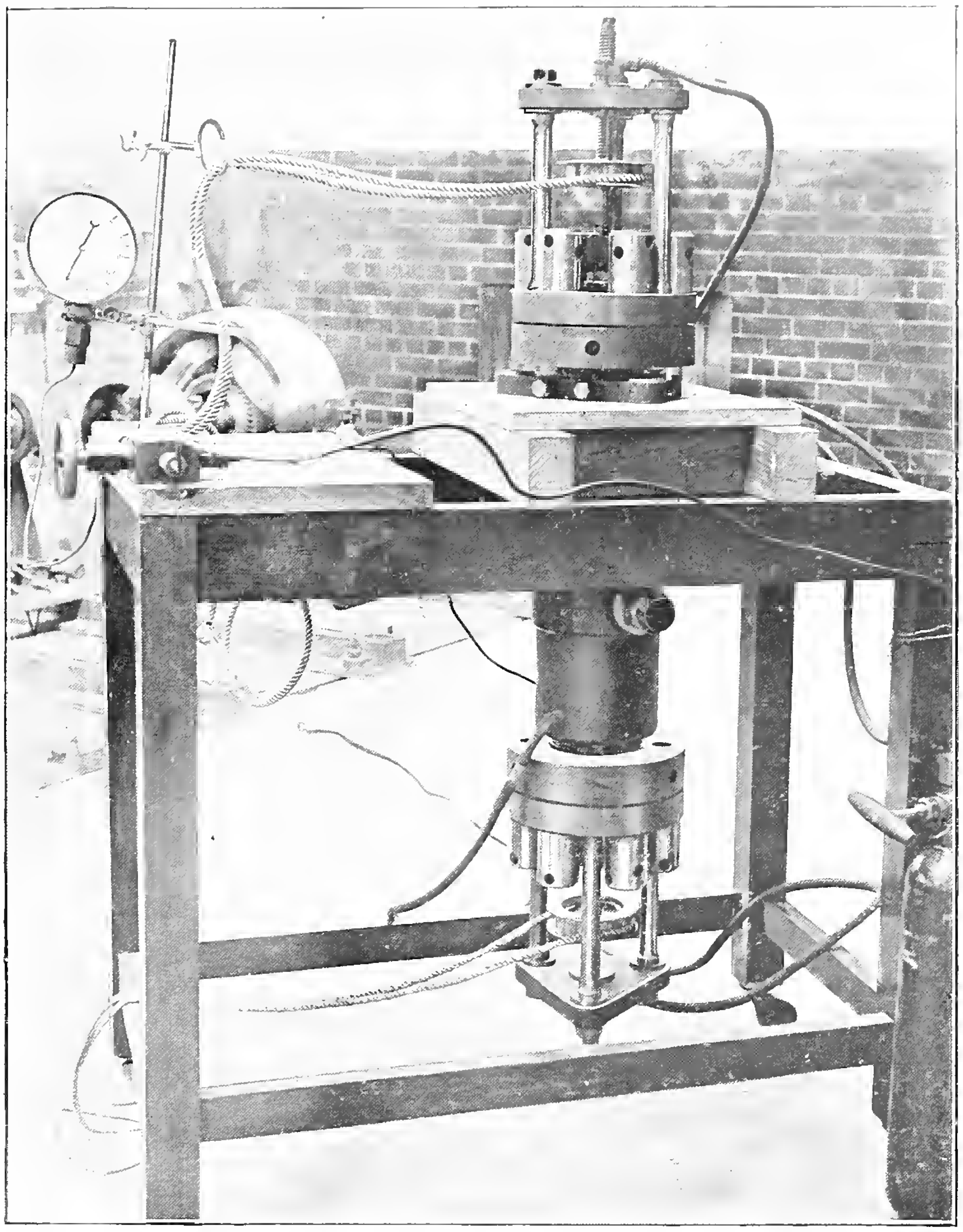


Fig. 1. Pressure cylinder and connections.

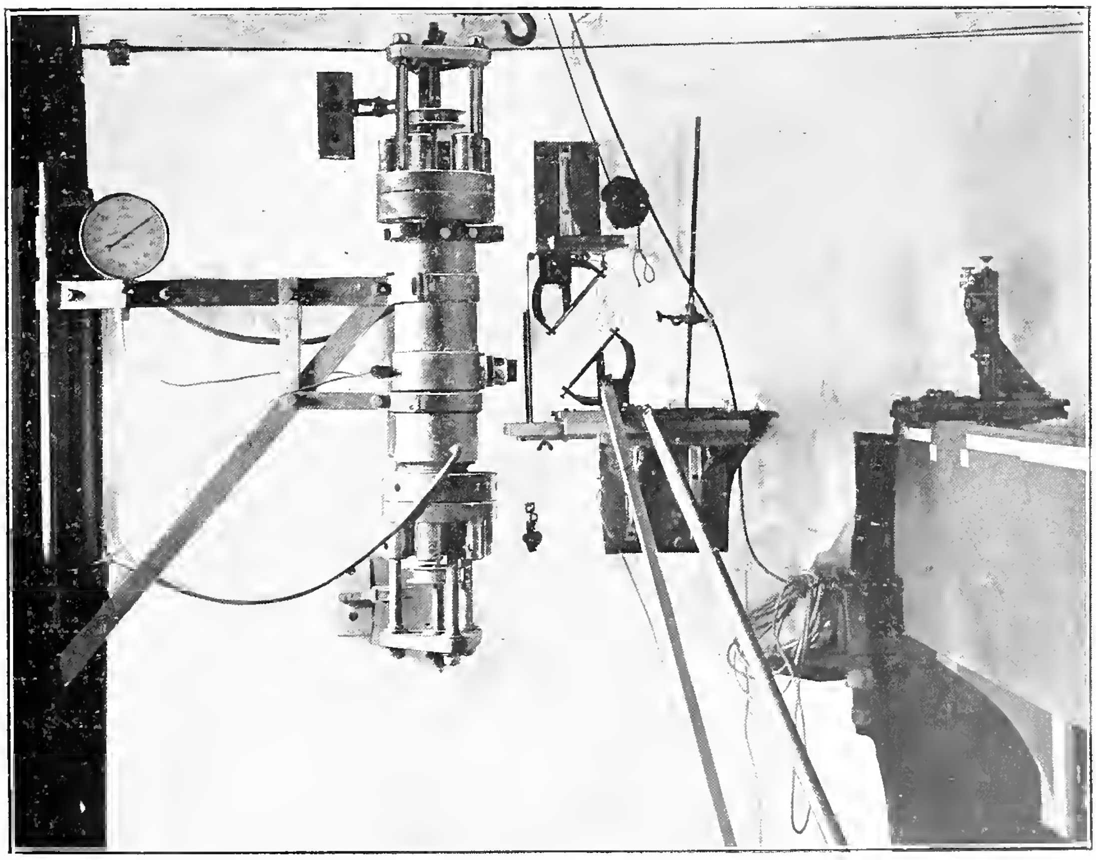
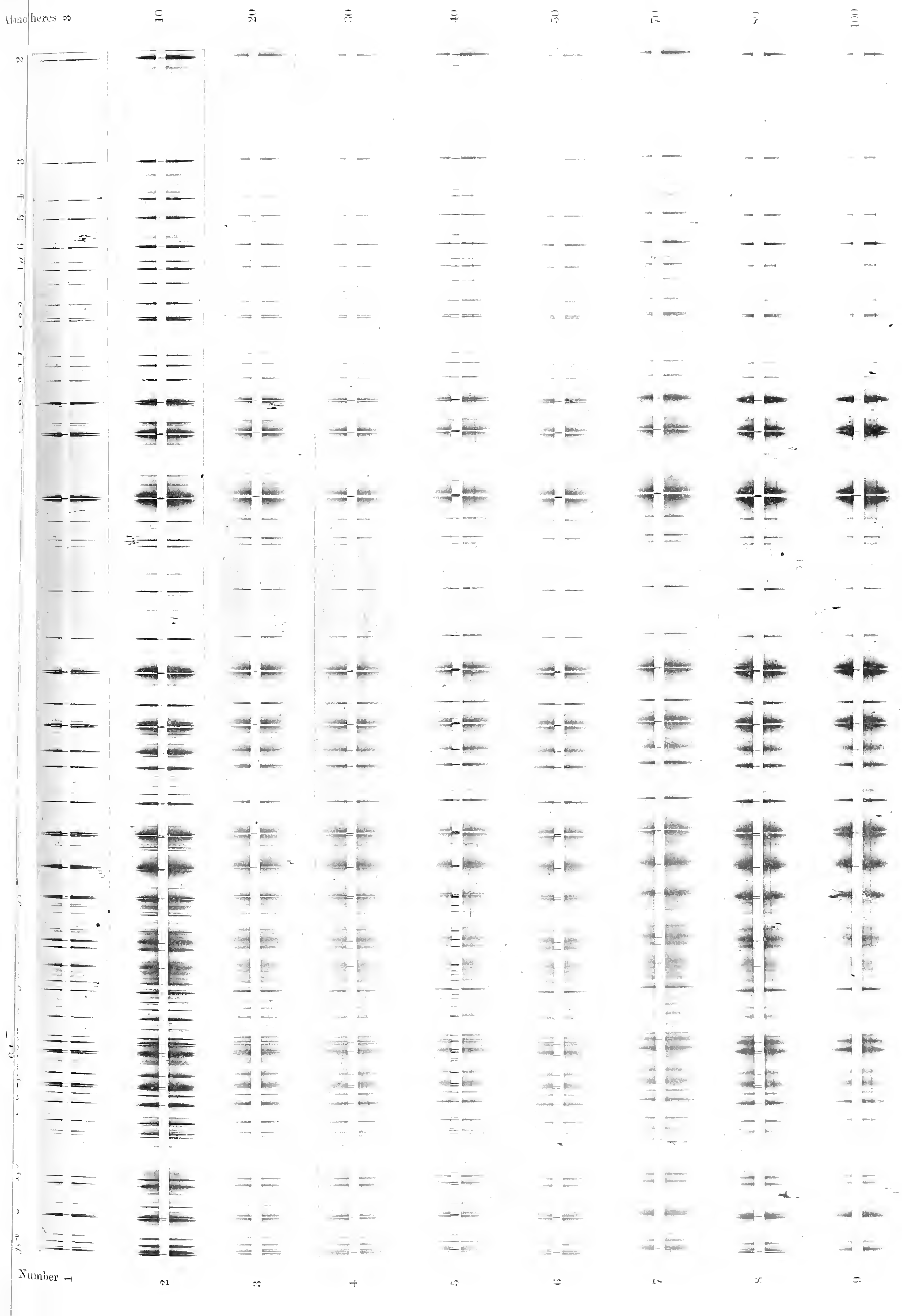


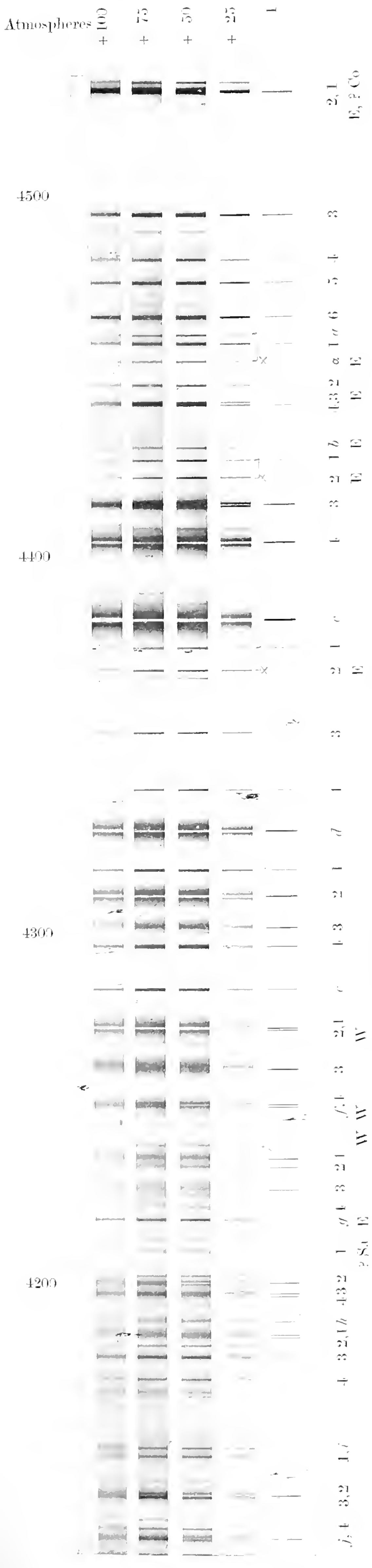
Fig. 2. Pressure cylinder and mirrors in position.

J. C. Duffield.

Phil. Trans., A, vol. 208, Plate 4.

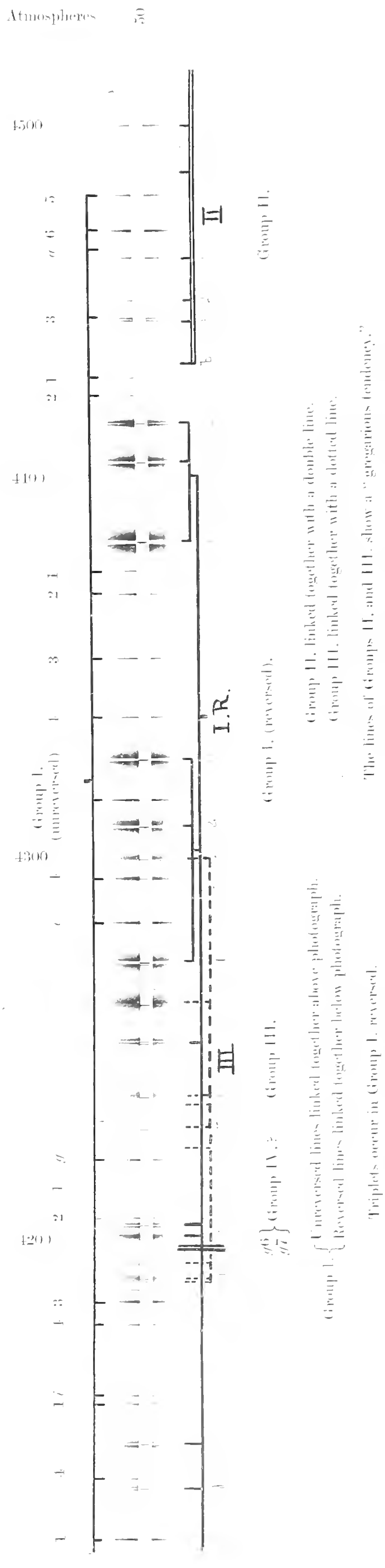


Negative (reduced). For wave-lengths corresponding to lettering, see pp. 136–138.



W = Weakened lines. E = Enhanced lines.

Fig. 1. Negative (reduced). For wave-lengths corresponding to lettering, see pp. 136–138.



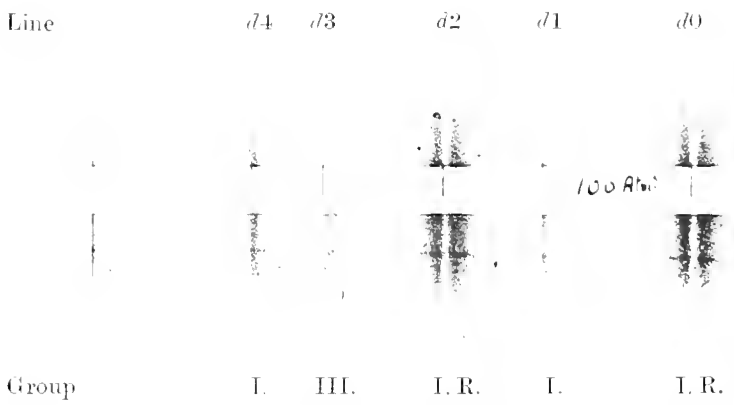
Group I. { Unreversed lines linked together above photograph.
Reversed lines linked together below photograph.

Triplets occur in Group I. reversed.

Group II. linked together with a double line.
Group III. linked together with a dotted line.

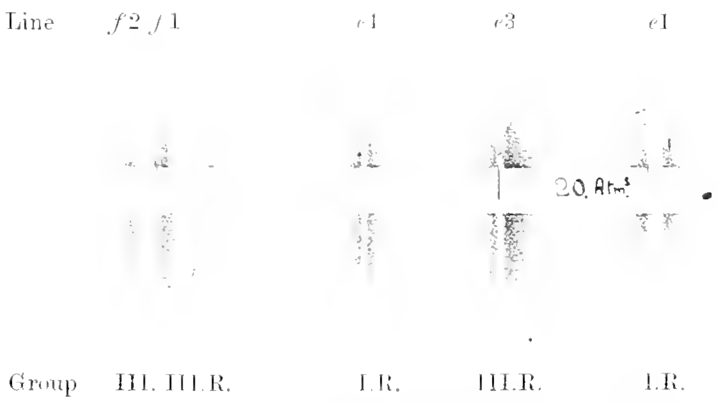
The lines of Groups II. and III. show a "gregarious tendency."

Fig. 2. Negative (reduced). For wave-lengths of the lines belonging to different groups, see Table X., p. 160.



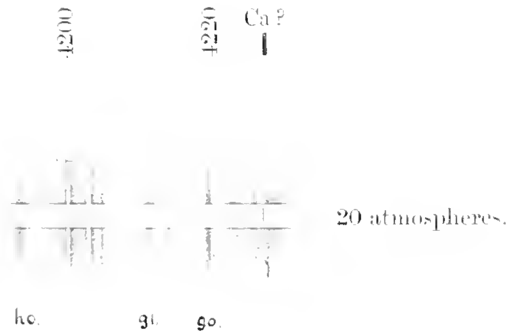
Line.	Wave-length.
*d*0	4325 ·19
*d*1	4315 ·21
*d*2	4307 ·96
*d*3	4299 ·12
*d*4	4294 ·26

Fig. 1. Negative (enlarged).



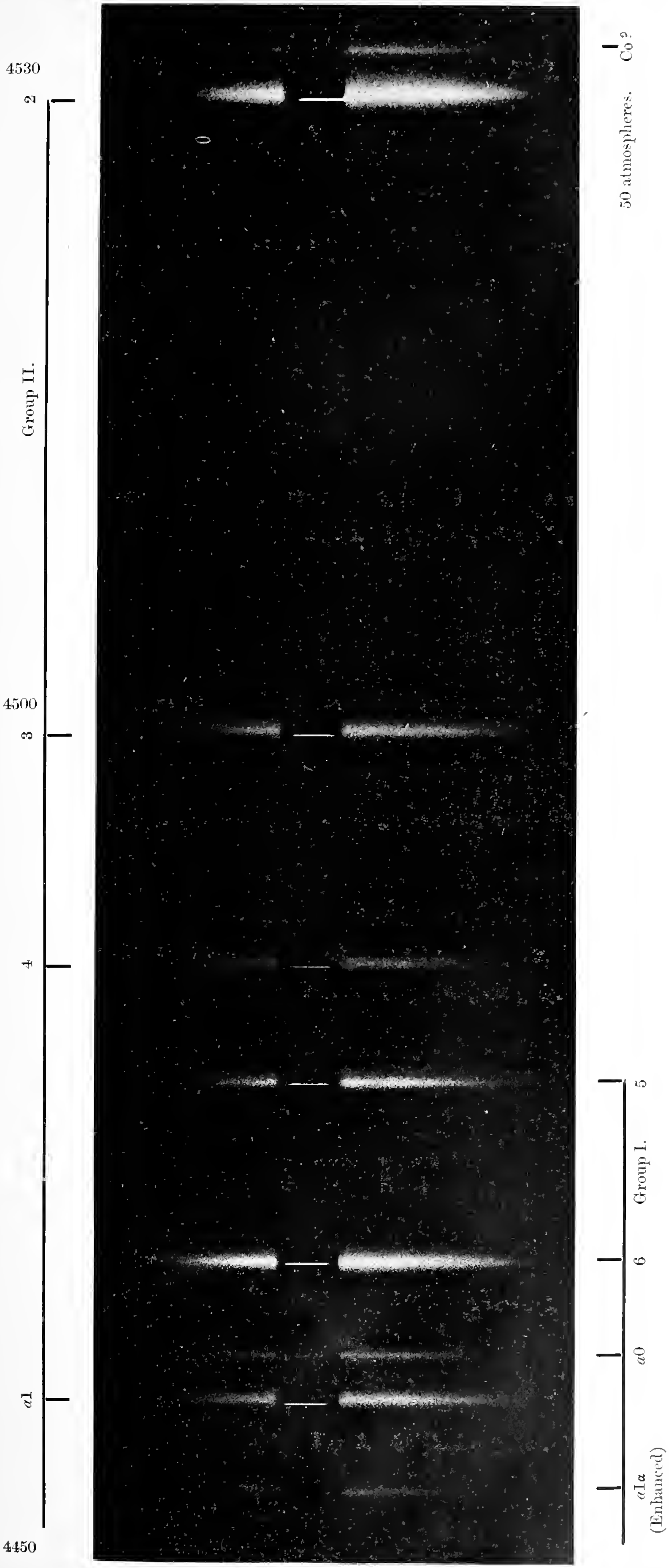
Line.	Wave-length.
*e*1	4271 ·39
*e*3	4260 ·64
*e*4	4250 ·93
*f*1	4236 ·09
*f*2	4233 ·76

Fig. 2. Negative (enlarged).



Line.	Wave-length.
Ca ?	4226 ·91
*g*0	4219 ·47
*g*1 ? Sa	4210 ·48
*h*0	4191 ·57

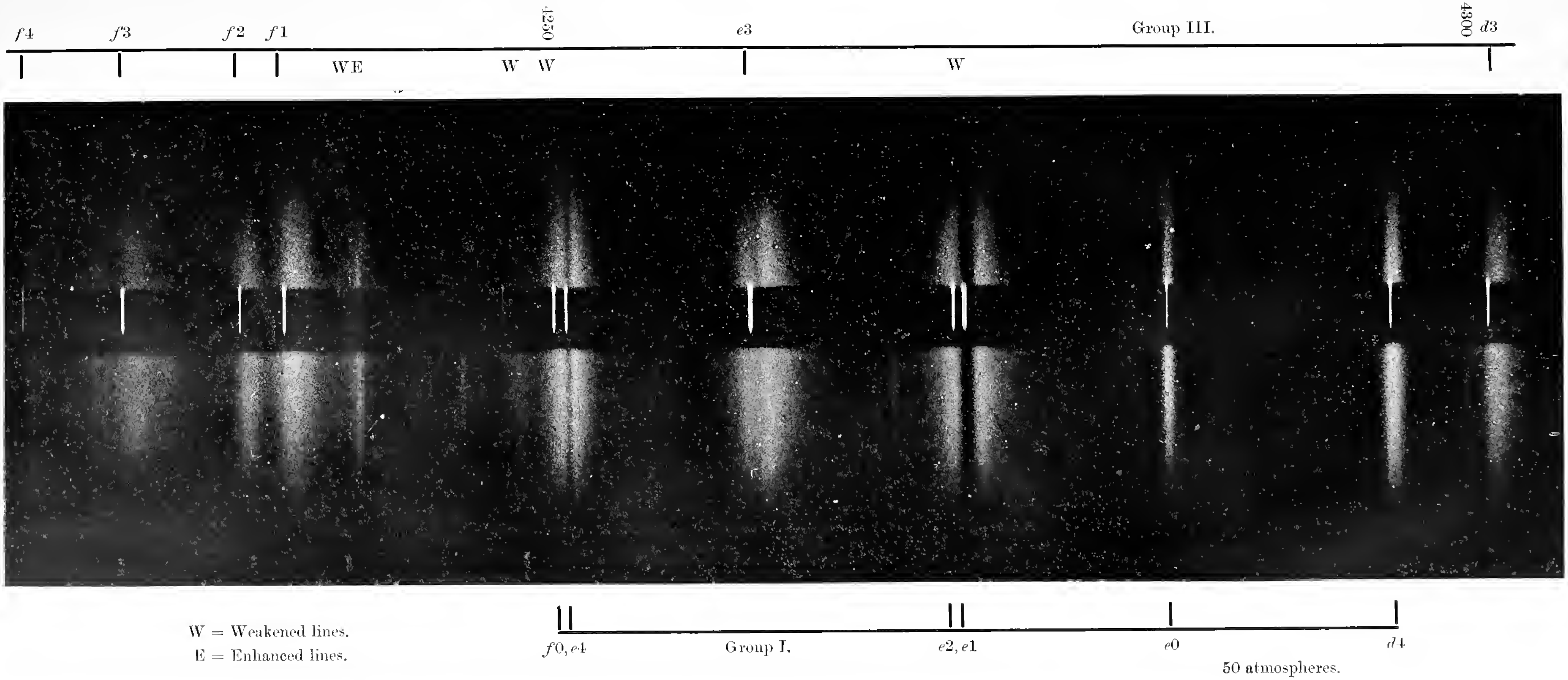
Fig. 3. Original negative.



Line.	Wave-length.
Co ?	4531·25
2	4528·78
3	4494·67
4	4482·35
5	4476·20

Line.	Wave-length.
6	4466·70
*a*0	4461·75
*a*1	4459·24
*a*1*a*	4454·50

Positive (enlarged).



W = Weakened lines.
E = Enhanced lines.

Line.	Wave-length.
d3	4299 ·42
d4	4294 ·26
e0	4282 ·58
e1	4271 ·93

Line.	Wave-length.
e2	4271 ·30
e3	4260 ·64
e4	4250 ·93
f0	4250 ·28

Line.	Wave-length.
f1	4236 ·09
f2	4233 ·76
f3	4227 ·60
f4	4222 ·32

Positive (enlarged).

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THE DIURNAL VARIATION OF TERRESTRIAL MAGNETISM

BY

ARTHUR SCHUSTER, F.R.S.

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IV. *The Diurnal Variation of Terrestrial Magnetism.*

By Arthur Schuster, *F.R.S.*

Received October 31,—Read November 7, 1907.

1. In a previous communication* I proved that the Diurnal Variation of Terrestrial Magnetism has its origin outside the earth's surface and drew the natural conclusion that it was caused by electric currents circulating in the upper regions of the atmosphere. If we endeavour to carry the investigation a step further and enquire into the probable origin of these currents, we have at present no alternative to the theory first proposed by Balfour Stewart that the necessary electromotive forces are supplied by the permanent forces of terrestrial magnetism acting on the bodily motion of masses of conducting air which cut through its lines of force. In the language of modern electrodynamics the periodic magnetic disturbance is due to Foucault currents induced in an oscillating atmosphere by the vertical magnetic force. The problem to be solved in the first instance is the specification of the internal motion of a conducting shell of air, which shall, under the action of given magnetic forces, determine the electric currents producing known electromagnetic effects. Treating the diurnal and semidiurnal variations separately, the calculation leads to the interesting results that each of them is caused by an oscillation of the atmosphere which is of the same nature as that which causes the diurnal changes of barometric pressure. The phases of the barometric and magnetic oscillations agree to about $1\frac{3}{4}$ hours, and it is doubtful whether this difference may not be due to uncertainties in the experimental data. In the previous communication referred to I already tentatively suggested a connexion between the barometric and magnetic changes, but it is only recently that I have examined the matter more closely. In the investigation which follows I begin by considering the possibility that both variations are due to one and the same general oscillation of the atmosphere. The problem is then absolutely determined if the barometric change is known, and we may calculate within certain limits the conducting power of the air which is sufficient and necessary to produce the observed magnetic effects; this conducting power is found to be considerable. It is to be observed, however, that the electric currents producing the magnetic variations circulate only in the upper layers of the atmosphere, where the pressure is too small to affect the barometer; the two

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* 'Phil. Trans.,' A, vol. 180, p. 467 (1889).

variations have their origin therefore in different layers, which may to some extent oscillate independently. Though we shall find that the facts may be reconciled with the simpler supposition of one united oscillation of the whole shell of air, there are certain difficulties which are most easily explained by assuming possible differences in phase and amplitude between the upper and lower layers. If the two oscillations are quite independent, the conducting power depending on the now unknown amplitude of the periodic motion cannot be calculated, but must still be large, unless the amplitude reaches a higher order of magnitude than we have any reason to assume.

The mathematical analysis is simple so long as we take the electric conductivity of the air to be uniform and constant; but the great ionisation which the theory demands requires some explanation, and solar radiation suggests itself as a possible cause. Hence we might expect an increased conducting power in summer and in daytime as compared with that found during winter and at night. Observation shows, indeed, that the amplitude of the magnetic variation is considerably greater in summer than in winter, and we know that the needle is at comparative rest during the night. The variable conducting power depending on the position of the sun helps us also to overcome a difficulty which at first sight would appear to exclude the possibility of any close connexion between the barometric and magnetic variations; the difficulty is presented by the fact that the change in atmospheric pressure is mainly semidiurnal, while the greater portion of the magnetic change is diurnal. This may to some extent be explained by the mathematical calculation, which shows that the flow of air giving a 24-hourly variation of barometric pressure is more effective in causing a magnetic variation than the corresponding 12-hourly variation, but the whole difference cannot be accounted for in this manner. If, however, the conductivity of air is greater during the day than during the night, it may be proved that the 12-hourly variation of the barometer produces an appreciable periodicity of 24 hours in the magnetic change, while there is no sensible increase in the 12-hourly magnetic change due to the 24-hourly period of the barometer. The complete solution of the mathematical problem for the case of a conducting power proportional to the cosine of the angle of incidence of the sun's rays is given in Part II. But even this extension of the theory is insufficient to explain entirely the observed increased amplitude of the magnetic variation during summer. We are, therefore, driven to assume either that the atmospheric oscillation of the upper layer is greater in summer than in winter and is to that extent independent of the oscillation of the lower layers, or that the ionising power of solar radiation is in some degree accumulative and that atmospheric conductivity is therefore not completely determined by the position of the sun at the time. The increased amplitude at times when sunspots are frequent is explained by an increased conductivity corresponding to an increase in solar activity. All indications, therefore, point to the sun as the source of ionisation, and ultra-violet radiation seems to be the most plausible cause.

2. The velocity potential of a horizontal irrotational motion of the earth's atmosphere considered as an infinitely thin shell is necessarily expressible as a series of spherical harmonics from which we may select for consideration the one of degree n and type σ, writing it $\psi_n^\sigma \sin\{\sigma(\lambda+t)-\alpha\}$ or ψ_n^σ according to convenience. The longitude λ is measured from any selected meridian towards the east, while t is the time of the standard meridian in angular measure. As in the greater part of the investigation λ and t occur in the combination $\lambda+t$ only, we may frequently omit t without detriment to the clearness, noting, however, that if the differentiation with respect to t is replaced by a differentiation with respect to λ we must apply the factor $2\pi/\mathrm{N}$, where N is the number of seconds in the day.

I consider in the first instance the electric currents which are induced in air moving horizontally under the influence of the earth's vertical magnetic force. Assuming the earth to be a uniformly magnetised sphere, its potential may be resolved into the zonal harmonic of the first degree and the tesseral harmonic of the first type and degree. The angle between the magnetic axis and the geographical axis not being great, the zonal harmonic constitutes by far the largest part, and forms the first subject of our investigation. As far as this part is concerned, we may put the vertical force equal to $\mathrm{C}\cos\theta$, where θ is the colatitude and C, measured upwards, has a numerical value differing little from $-\frac{2}{3}$.

The components of electric force, X and Y, measured towards the south and east respectively, are

$$\mathrm{X}a = \mathrm{C}\cot\theta\frac{d\psi}{d\lambda},\qquad \mathrm{Y}a = -\mathrm{C}\cos\theta\frac{d\psi}{d\theta}\quad\ldots\ldots\ldots\quad(1),$$

and these equations may be written in the form

$$\left.\begin{aligned} n\,.\,n+1\,.\,\mathrm{X}a &= \mathrm{C}\frac{d^2\psi}{d\theta\,d\lambda}+\mathrm{C}\frac{d}{\sin\theta\,d\lambda}\left(n\,.\,n+1\,.\,\psi\cos\theta-\sin\theta\frac{d\psi}{d\theta}\right)\\ n\,.\,n+1\,.\,\mathrm{Y}a &= \mathrm{C}\frac{d^2\psi}{\sin\theta\,d\lambda^2}-\mathrm{C}\frac{d}{d\theta}\left(n\,.\,n+1\,.\,\psi\cos\theta-\sin\theta\frac{d\psi}{d\theta}\right)\end{aligned}\right\}\quad\ldots\quad(2),$$

where n is the degree of the harmonic.

The identity between (1) and (2) is obvious as regards the first of the equations, and the reduction of the second is obtained with the help of the fundamental equation

$$\sin\theta\frac{d}{d\theta}\sin\theta\frac{d\psi}{d\theta}+\frac{d^2\psi}{d\lambda^2}+n\,.\,n+1\,.\,\sin^2\theta\,.\,\psi = 0,$$

ψ being a zonal harmonic of degree n.

The components of electric force are by (2) reduced to the form

$$\mathrm{X} = -\frac{d\mathrm{S}}{a\,d\theta}+\frac{d\mathrm{R}}{a\sin\theta\,d\lambda};\qquad \mathrm{Y} = -\frac{d\mathrm{S}}{a\sin\theta\,d\lambda}-\frac{d\mathrm{R}}{a\,d\theta}\quad\ldots\ldots\quad(3),$$

and may be divided into two portions, the first of which is derivable from a potential

$$\mathrm{S} = -\mathrm{C}\frac{d\psi}{d\lambda}\Big/ n \,.\, (n+1).$$

In the steady state this part is balanced by a static distribution of electricity revolving round the earth and causing a variation in the electrostatic potential which is found to be too weak to affect our instruments. The second portion of the electric force produces electric currents; these, neglecting electric inertia—which will be considered later—have $\rho\mathrm{R}$ as current function, where ρ is the conductivity of the medium.

The comparison of (2) and (3) shows that

$$n \,.\, n+1 \,.\, \mathrm{R} = \mathrm{C}\left(n \,.\, n+1 \,.\, \psi \cos\theta - \frac{d\psi}{d\theta}\sin\theta\right),$$

and by means of well known reductions R may be expressed in the normal form

$$(2n+1)\, n \,.\, n+1 \,.\, \mathrm{R} = \mathrm{C}\left[n^2(n-\sigma+1)\,\psi_{n+1} + (n+1)^2(n+\sigma)\,\psi_{n-1}\right]. \quad . \quad . \quad (4).$$

Here ψ_{n+1} and ψ_{n-1} are the two spherical harmonics of degree n and type σ which have the same numerical factor as the current function ψ_n.

I shall confine myself to the two principal portions of the diurnal variation of barometric pressure which are associated with the velocity potentials

$$\psi_1{}^1 = \mathrm{A}_1 \sin\theta \sin\{(\lambda+t)-\alpha_1\} \quad \text{and} \quad \psi_2{}^2 = 3\mathrm{A}_2 \sin^2\theta \sin\{2(\lambda+t)-\alpha_2\}.$$

The corresponding electric current functions are seen by (4) to be

$$\rho\mathrm{R}_2{}^1 = \tfrac{1}{6}\rho\mathrm{C}\mathrm{A}_1\psi_2{}^1 \quad \text{and} \quad \rho\mathrm{R}_3{}^2 = \tfrac{2}{15}\rho\mathrm{C}\mathrm{A}_2\psi_3{}^2 \,. \quad . \quad . \quad . \quad . \quad . \quad (5).$$

It is shown by CLERK MAXWELL ('Electricity and Magnetism,' vol. II., p. 281) that the magnetic forces accompanying the currents in spherical sheets which are derivable from a current function having the form of a surface harmonic are obtained from a magnetic potential which is equal to the same harmonic multiplied by a factor which inside the spherical shell is $-4\pi(n+1)\,r^n/(2n+1)\,a^n$. The thickness of the atmosphere being negligible compared with the radius of the earth, we may put $r = a$, and obtain thus, for the magnetic potential Ω due to the induced electric currents,

$$-\Omega = \left[\tfrac{2}{5}\mathrm{A}_1\psi_2{}^1 \sin\{(\lambda+t)-\alpha_1\} + \tfrac{32}{105}\mathrm{A}_2\psi_3{}^2 \sin\{2(\lambda+t)-\alpha_2\}\right]\pi\rho e\mathrm{C} \quad . \quad . \quad (6).$$

The quantity e represents the thickness of the shell of the conducting layer, and is introduced because the current functions used above yield current densities, while MAXWELL'S result applies to functions which lead directly to currents. Our equation (6) represents the potential of the diurnal variation of terrestrial magnetism calculated from an atmospheric oscillation according to our theory, and agrees in form with the principal terms of that variation as observed when the average annual value is considered and the seasonal changes are disregarded.

3. It remains to be seen whether the calculated variation agrees as regards phase and can be made to coincide in magnitude by a reasonable value of the conductivity and thickness of the effective layers of the atmosphere.

For this purpose we first obtain a value for the constants A_1 and A_2. If δp be the variation of the pressure p, and $d\sigma$ the corresponding change of the density σ, we have

$$\frac{\delta p}{p} = \frac{d\sigma}{\sigma} = -\frac{d\psi}{v^2 dt},$$

where ψ is the velocity potential and v the velocity of sound. Under the assumption that the whole atmosphere oscillates equally in all its layers, $\delta p/p$ will be the same at every point of a vertical line, and we may, therefore, determine its value at the surface of the earth.

According to HANN ('Meteorologie,' p. 189), the diurnal change of the barometer at the equator, measured in millimetres, is represented by

$$0{\cdot}3 \sin(\lambda + t) + 0{\cdot}92 \sin\{2(\lambda + t) + 156^\circ\}.$$

If this expression be denoted by δp, we must assign the value of 760 to p to bring the units into harmony.

It follows that at the equator

$$\psi = [-0{\cdot}3 \cos(\lambda + t) + 0{\cdot}46 \cos\{2(\lambda + t) + 156^\circ\}]\, \mathrm{N}v^2/2\pi p \quad . \quad . \quad . \quad (7).$$

The numerical value of $\mathrm{N}v^2/2p$ is $6{\cdot}281 \times 10^{10}$ ($\mathrm{N} = 86400$; $v^2 = 11{\cdot}05 \times 10^8$), or $98{\cdot}5a$, where a is the radius of the earth.

The constants A_1 and A_2 of the velocity potential in (6) are, therefore, determined by

$$\pi A_1 = 0{\cdot}3 \times 98{\cdot}5a = 29{\cdot}6a, \quad \text{and} \quad \pi A_2 = 0{\cdot}153 \times 98{\cdot}5a = 15{\cdot}1a \quad . \quad . \quad (8).$$

We ultimately get for the calculated magnetic potential

$$\Omega/a = [11{\cdot}8 \cos(\lambda + t) - 4{\cdot}6 \cos 2(\lambda + t - 102^\circ)]\, \rho e \mathrm{C},$$

or, introducing the value of C and restoring the term containing the latitude,

$$\Omega/a = [7{\cdot}89 \psi'_2 \cos(\lambda + t - 180^\circ) + 3{\cdot}07 \psi_3^2 \cos 2(\lambda + t - 102^\circ)]\, \rho e \quad . \quad . \quad (9).$$

The principal terms of the diurnal and semidiurnal variations of magnetic force, abstraction being made of seasonal changes, were found in my previous communication to be

$$10^6 \Omega/a = 89 \psi_2' \cos(\lambda + t - 156^\circ) + 11{\cdot}16 \psi_3^2 \cos 2(\lambda + t - 74{\cdot}5^\circ) \quad . \quad . \quad (10).$$

If we compare the phases, we find that the magnetic potential calculated from the barometric variation lags behind the observed one by an amount which is 1 hour and 36 minutes for the diurnal and 1 hour and 50 minutes for the semidiurnal variation, showing a remarkably close agreement in the two terms. As regards amplitude, we can establish agreement by adjusting the value of ρe, but the same value ought to satisfy both terms, which is not the case, ρe being $3{\cdot}63 \times 10^{-6}$ if calculated from the 12-hourly variation, and $11{\cdot}3 \times 10^{-6}$ if calculated from the 24-hourly variation.

4. The tacit assumption has been made that the barometric variation is distributed over the surface of the earth according to the simplest harmonic term consistent with each period, so that for the diurnal variation the amplitude would be proportional to the cosine of the latitude, and for the semidiurnal variation to the square of the cosine.

The experimental data show, however, that there are other terms to be considered, and for the semidiurnal variation Dr. ADOLF SCHMIDT has obtained the best agreement by introducing the harmonic of the fourth degree, having an amplitude which at the equator would amount to the twelfth part of the whole effect. The amplitude of the second term in Equation 9 would consequently be reduced to $3{\cdot}07 \times \frac{11}{12} = 2{\cdot}814$, and a higher harmonic would be introduced; but the experimental evaluation of these higher terms in the magnetic variation is too uncertain to be taken account of at present, their effect in any case being small. As regards the 24-hourly variation, its dependence on latitude has not been clearly established. The term, as commonly observed, is much affected by local circumstances, and HANN takes therefore the observation on board ship to represent the true phenomenon so far as it depends on the atmosphere as a whole. While greater consistency is thus gained, the observations on board ship cannot lay claim to the same accuracy as those taken on land, and, as the figures show, considerable uncertainty still prevails. In the following table the values given by HANN are collected together:—

Latitude.	Amplitude in millimetres.	Latitude.	Amplitude in millimetres.
°		°	
4·5	0·262	33·8	0·148
11·1	0·265	35·9	0·140
15·8	0·268	37	0·342
23	0·115	40·7	1·85

These numbers do not follow any very simple law and can only be very partially represented by an expression varying as the cosine of the latitude. The rapid increase in the amplitude at latitudes of about 40° suggests the presence of the third harmonic, and treating the figures by the method of least squares we are led to an expression

$$\delta p = 0{\cdot}49 \sin\theta - 0{\cdot}33 \left\{\tfrac{3}{2} \sin\theta \left(5 \cos^2\theta - 1\right)\right\}.$$

If this equation were to represent correctly the distribution in latitude of the diurnal term, the calculated amplitude of the magnetic potential would be increased considerably more than is required to bring it into harmony with the semidiurnal term, because not only is the amplitude of the term of the barometric variation in $\sin\theta$ increased, but the additional term gives rise to a magnetic potential which is of the same degree and type and more than doubles the effect of the first term.

Very little importance, however, can be attached to this calculation, which depends to a great extent on the last entry of the foregoing table; but enough has been said to show that our present knowledge of the 24-hourly variation of the barometric pressure is very uncertain, and that a term of the third degree in its expression is likely to diminish materially the discrepancy between the electric conductivity of the atmosphere as derived from the diurnal and semidiurnal periods.

5. We must next turn our attention to several corrections which modify the calculated values without, however, introducing material changes. The observed magnetic variations have been treated as if they were wholly due to outside causes, although it was shown in my previous communication that an appreciable portion of it was an effect of electric currents induced inside the earth by the varying potential itself. What we observe is the resultant of the original outside effect and its concomitant induced inside effect. To explain the absence of time lag of the induced variation it was necessary to assume a good conductivity of an inner core and small conductivity of the outer shell. An estimate may be made of the radius of the conducting core. If the outer potential is represented by $\Omega r^n a^{-n}$, where a is the radius of the earth, and the inner potential is $\kappa\Omega r^{-n-1}a^{n+1}$, an estimate of κ may be obtained by the fact that if the inner conductivity is sufficiently great the vertical force is entirely destroyed at the surface of the inner core. If this has a radius r_0, it follows that $nr_0{}^n a^{-n}$ and $(n+1)\kappa r_0{}^{-n-1}a^{n+1}$ must have equal values, or that $\kappa = nr_0{}^{2n+1}/(n+1)\,a^{2n+1}$.

The resultant potential at the surface of the earth is, therefore,

$$\Omega\left[1+\frac{n}{n+1}\left(\frac{r_0}{a}\right)^{2n+1}\right].$$

If this expression is multiplied by n, we obtain the vertical force calculated from the horizontal force on the supposition that the whole effect comes from the outside.

The *observed* vertical force, on the other hand, is

$$n\Omega\left[1-(r_0/a)^{2n+1}\right].$$

The previous result showed that the actual vertical force was about half the calculated one, the principal term being that due to $n = 2$. We find in this way $(r_0/a)^5$.

The thickness of the outer non-conducting crust would thus appear to be about 1000 kilometres, and cannot, therefore, be connected with the layer having a thickness of about 30 miles which shows itself in its effect on seismic waves, and, according to STRUTT, contains the radioactive matter. On the other hand, it is quite likely that the outer shell is identical with that which the discussion of the propagation of seismic waves shows to have different elastic properties from the nucleus, and which, according to WIECHERT'S recent researches, has a thickness of 1500 kilometres.

The observations show that the internal potential has a value equal to one-fourth of the external one, or that the external potential represents 0·8 of the whole. For $n = 3$, using the same value of r_0, we similarly find that the outside effect is 0·84 times that of the whole. The coefficients in equation (9) should therefore be diminished by multiplying with 0·80 and 0·84 respectively.

6. We may now complete the investigation as far as it relates to uniform conductivities. The magnetic and geographical poles of the earth not coinciding, the vertical force is not simply proportional to the cosine of the colatitude, but a term must be added proportional to $\sin\theta\cos\lambda$, where λ is measured from the meridian 68° 31′ west of Greenwich, which is that containing the magnetic axis. I discuss the effect of the inclination of the magnetic axis somewhat in detail, as it will give us a good test of the proposed theory when suitable observations will be available. Leaving out the factor $C\tan\phi$, where C represents the vertical force at the geographical pole and ϕ the colatitude of the magnetic pole, the electric forces, as far as they concern us at present, are

$$X = \cos\lambda\frac{d\psi}{d\lambda}; \quad Y = -\sin\theta\cos\lambda\frac{d\psi}{d\theta}.$$

If these values be substituted in (3), the elimination of S leads to the equation

$$\frac{d}{d\lambda}\cos\lambda\frac{d\psi}{d\lambda} + \frac{d}{d\theta}\sin^2\theta\cos\lambda\frac{d\psi}{d\theta} = \frac{d^2\mathrm{R}}{\sin\theta\, d\lambda^2} + \frac{d}{d\theta}\sin\theta\frac{d\mathrm{R}}{d\theta}. \quad . \quad . \quad (11).$$

It will be shown in Part II. that

$$\left(\frac{d}{d\lambda}\cos\lambda\frac{d}{d\lambda} + \cos\lambda\frac{d}{d\theta}\sin^2\theta\frac{d}{d\theta}\right)\psi_n{}^\sigma\sin\sigma(\lambda+t-\alpha)$$

is equal to

$$\tfrac{1}{2}\frac{\sin\theta}{2n+1}\left[(a_1\psi_{n-1}{}^{\sigma+1}+b_1\psi_{n+1}{}^{\sigma+1})\sin\{\sigma(\lambda+t)+\lambda-\alpha\}\right.$$
$$\left.+(a_2\psi_{n-1}{}^{\sigma-1}+b_2\psi_{n+1}{}^{\sigma-1})\sin\{\sigma(\lambda+t)-\lambda-\alpha\}\right],$$

where

$$a_1 = n-1\,.\,n+1; \quad -b_1 = n\,.\,n+2; \quad -a_2 = (n-1)(n+1)(n+\sigma)(n+\sigma-1);$$
$$b_2 = n\,.\,n+2\,.\,(n-\sigma+1)\,.\,(n-\sigma+2).$$

The only case necessary to consider is that in which $n = \sigma$, when $\phi_{n-1}{}^{\sigma+1} = 0$, so that we may disregard the factor a_1. If $n = \sigma = 1$, then $b_1 = -3$; $a_2 = 0$; $b_2 = 6$; and if $n = \sigma = 2$, then $b_1 = -8$; $a_2 = -36$; $b_2 = 16$.

We can satisfy equation (3) by assuming R to be made up of two or four terms, according as we treat of the diurnal or semidiurnal variations. Remembering that by the fundamental equation

$$\left(\frac{d^2}{\sin\theta\, d\lambda^2}+\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}+n\,.\,n+1\right)\psi_n^{\sigma}=0,$$

we find the terms which are introduced by the inclination of the magnetic axis to be for the diurnal variation

$$\tfrac{1}{12}\mathrm{R}_2^{\,2}\sin(2\lambda+t-\alpha)-\tfrac{1}{6}\mathrm{R}_3^{\,0}\sin(t-\alpha),$$

and for the semidiurnal variation

$$\tfrac{1}{15}\mathrm{R}_3^{\,3}\sin(3\lambda+2t-\alpha)+\tfrac{9}{5}\mathrm{R}'_1-\tfrac{2}{15}\mathrm{R}'_3)\sin(\lambda+2t-\alpha).$$

The additional terms are therefore, restoring the constant factor,

$$\begin{aligned}-\Omega = -[\tfrac{1}{5}\mathrm{A}_1\psi_2^{\,2}\sin(t'+\lambda-\alpha_1)-\tfrac{2}{5}\mathrm{A}_1\psi'_2\sin(t'-\lambda-\alpha_1)+\tfrac{16}{5}\mathrm{A}_2\psi_3^{\,3}\sin(2t'+\lambda-\alpha_2)\\ +(\tfrac{24}{5}\psi'_1-\tfrac{32}{105}\psi'_3)\,\mathrm{A}_2(\sin 2t'-\lambda-\alpha_2)]\,\pi\rho e\mathrm{C}\tan\phi \quad . \quad . \quad . \quad . \quad . \qquad (12).\end{aligned}$$

Here tan ϕ represents the angle between the magnetic and geographical axes ($\tan\phi = 0{\cdot}202$), and t' has been introduced to represent the local time $\lambda+t$. The functions ψ are the tesseral functions, so that

$$\psi_2^{\,0}=\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2},\qquad \psi'_3=\tfrac{3}{2}\sin\theta\,(5\cos^2\theta-1),\qquad \psi'_1=\sin\theta,$$
$$\psi_2^{\,2}=3\sin^2\theta,\qquad \psi_3^{\,3}=15\sin^3\theta.$$

Equations (12) show that if the inclination of the magnetic axis be taken into account, the diurnal variations do not entirely depend on local time. A barometric variation of a certain period is accompanied by a magnetic variation of the same period, as is obvious; but if the lines of equal magnetic potential in the diurnal variation are drawn as in my previous communication, a barometric variation represented by $\psi_n^{\sigma}\cos\sigma t$ results in a magnetic potential containing terms

$$\psi_{n-1}^{\,\sigma-1}\cos(\sigma-1)\,\lambda\,;\quad \psi_{n+1}^{\,\sigma-1}\cos(\sigma-1)\,\lambda\,;\quad \psi_{n-1}^{\,\sigma+1}\cos(\sigma+1)\,;\quad \psi_{n+1}^{\,\sigma+1}\cos(\sigma+1)\,\lambda.$$

These equipotential lines and their coincident stream lines revolve with velocities $\sigma\omega/\sigma-1$ and $\sigma\omega/(\sigma+1)$ round the earth, ω being its angular velocity, and in this way variations proportional to cos σt are produced.

In order to estimate the magnitude of these terms, consider the diurnal variation, the normal term of which has been found to be equal to $\tfrac{4}{5}\mathrm{A}_1\psi'_2\cos(t-\alpha)$.

Along a meridian circle for which λ is either 0 or π, the additional terms are, putting A_1 equal to unity, for $\lambda = 0$

$$[\tfrac{3}{10}\sin^2\theta-\tfrac{1}{10}(3\cos^2\theta-1)]\cos(t-\alpha)=\tfrac{1}{10}(1-3\cos 2\theta)\cos(t-\alpha),$$

and for $\lambda = \pi$

$$\left[\tfrac{3}{10}\sin^2\theta+\tfrac{1}{2}(3\cos^2\theta-1)\right]\cos(t-\alpha) = \tfrac{1}{5}\cos(t-\alpha).$$

In these equations the numerical value 0·2 has been introduced for tan ϕ.

At the equator the additional terms, therefore, have amplitudes $\frac{2}{5}$ and $\frac{1}{5}$ respectively, as compared with the main diurnal term. The force to geographical west being proportional to the potential, we may take these numbers to be the amplitude of the westerly force variations. The main variation is proportional to $\sin\theta\cos\theta$, and has zero value at the equator in the tropical region. The additional terms are therefore the ruling terms at the equator. The horizontal force along the same circle has unit amplitude, measured on the same scale, so that the new terms come well within the range of our observational powers. It would be interesting to trace them, but it should be remarked that only observations made near the equinox are suitable for the purpose, as the seasonal terms, which yet remain to be discussed, would otherwise interfere.

7. We may interrupt the progress of our investigation for a moment to inquire into the magnitude of the electrostatic effect dependent on the potential S which was found equal to $-\mathrm{C}\dfrac{d\psi}{d\lambda}\Big/n\,.\,n+1$, leading to a vertical electric force $\mathrm{C}\sigma\psi/(n+1)\,a$. In the two cases which concern us, $\sigma = n$, and ψ has values at the equator which were found to be $30a/\pi$ and $15\,a/\pi$ respectively. It follows that the variation of vertical electric force is of the order of 3 C.G.S. units, which is only 1 volt per 300 kilometres. This may be disregarded.

8. The previous discussion has only taken the earth's vertical magnetic force into consideration. The horizontal force causes, in combination with a horizontal atmospheric oscillation, a vertical electromotive force, and so far as this produces electric currents, their flow is in opposite directions in strata which are vertically above each other. The magnetic effect is therefore of a smaller order of magnitude than that due to vertical force.

9. In calculating the currents from the electric forces, I have applied OHM's law, and therefore neglected the effects of electric inertia; but it is not difficult to estimate the change of phase which results from self-induction. Using the equations given by MAXWELL* for spherical current sheets, we find that if R is the function defined by equation (3), and ϕ the current function,

$$\phi+\mathrm{L}\rho\frac{d\phi}{dt} = \mathrm{R}\rho,$$

where ρ is the conductivity, and $\mathrm{L} = (2n+1)/4\pi a$; provided that R is a surface harmonic of degree n. If the latter function is proportional to $\cos\kappa t$, we find in the usual way

$$\phi = \rho\cos\epsilon\cos(\kappa t-\epsilon),\quad \tan\epsilon = \frac{4\pi a\kappa\rho}{2n+1}.$$

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* See CLERK MAXWELL, 'Electricity and Magnetism,' vol. II., § 672.

If we take the current sheets to be of finite thickness e, and ρ denotes conductivity referred to unit volume, we must write

$$\tan \epsilon = \frac{4\pi a\kappa\rho e}{2n+1}.$$

If ρe has the value previously determined by the semidiurnal variation, I calculate a retardation of 1 hour for the semidiurnal and about $1\frac{1}{2}$ hours for the diurnal term. The amplitude would be reduced by about 14 per cent. There are various causes, notably the inequalities of conductivity, tending to diminish the retardation, so that we may consider that self-induction would not cause a shift of phase amounting to more than an hour, but it is in the opposite direction to that indicated by the observations, if the barometric and magnetic oscillations are due to identical causes.

10. It is known that the air contains an excess of positive electricity, and the question might be raised whether the oscillations of the atmosphere do not convectively produce direct magnetic effects. If E be the total quantity of electricity contained in a vertical column of unit cross section, and V, the velocity of air in that column, supposed to be uniform, the total current in the atmosphere across a vertical area of unit width is EV, and the magnetic force at the surface of the earth is of the order of magnitude 2πEV. The quantity E must be equal and opposite to the surface electrification of the earth, which itself is equal to $F/4\pi v^2$, where v is the velocity of light, and F the normal fall of potential, which we may put equal to 1 volt per centimetre, or to 10^8. The magnetic force has therefore a magnitude of order $5{\cdot}8V \times 10^{-14}$. If the velocity potential of the atmospheric oscillation is $A\psi_n^\sigma \sin \sigma (\lambda + t)$, the velocity in the two cases considered is greatest at the equator, where its maximum rises to $\sigma A\psi_n^\sigma/a$, which for the diurnal and semidiurnal change is A_1/a and $6A_2/a$ respectively. It follows from the numerical values given in (8) that the maximum equatorial velocities are 10 and 30 centims. per second respectively. The magnetic forces due to such velocities are quite insignificant. In the literature referring to the subject we frequently find it suggested that magnetic disturbances are due to moving masses of electrified air, some writers even going so far as to say that this has been *proved*; it may be demonstrated, on the contrary, that the assumed cause is insufficient. For horizontal air currents this has just been demonstrated, and the effects of ascending or descending currents are still less efficient. If a column of air of cylindrical shape having as base a circle of radius r rises or falls with velocity V, and it is imagined as an extreme case that the column extends indefinitely in both directions, the magnetic force at the boundary is $2\pi r$EV, where E is the electric density. At the surface of the earth the ionisation is such that the free electric charges of each kind amount to about 1 electrostatic unit per cubic metre. Let us assume one kind to be suppressed altogether, so that this number represents the electric volume density, or in electromagnetic measure $0{\cdot}33 \times 10^{-16}$. If r be 1 kilometre, and the velocity that of an express train, or 30 metres a second, the

magnetic effect would be $6{\cdot}3\times10^{-8}$ C.G.S. This is insignificant and leaves a good margin for a greater sectional area of the ascending current, especially if it is remembered that both our assumed velocity and the volume charges are many times greater than is allowable. Magnetic effects due to the motion of electrified air must therefore be ruled out as effective causes of either regular or irregular magnetic changes.

11. The daily variation of the magnetic forces includes a strong seasonal term, the amplitudes being greater in summer than in winter. In order to explain this term according to the theory advocated, it is necessary to assume a greater electric conductivity of the atmosphere in summer than in winter, or an oscillation of greater amplitude, which is not, however, indicated by the barometric changes. That the conductivity depends on the position of the sun, and may therefore vary with the season, is suggested by the relation in phase between the diurnal and semidiurnal terms, these terms combining together so as to leave the needle comparatively quiescent during the night. Reserving the possible causes of the conductivity and its dependence on solar position for further discussion, we may complete the theoretical investigation by introducing a variable conductivity. The simplest supposition to make will be that the conducting power in any small volume is proportional to the cosine of the angle between the vertical and the line drawn to the sun, or, in other words, proportional to the cosine of the angle, measured at the centre of the earth on the celestial sphere, between the sun and the small volume considered. This angle (ω) is expressed in spherical co-ordinates by

$$\cos\omega = \sin\delta\cos\theta + \sin\theta\cos\delta\cos\lambda \quad \ldots\ldots \quad (13),$$

where λ is the longitude measured from the meridian passing through the sun, and θ is measured from the pole, δ representing the sun's declination. To put the assumed law of conductivity into mathematical form, we write

$$\rho = \rho_0 + \rho_1 \cos\omega.$$

If $\rho_1 = \rho_0$, the conductivity would be zero at a point opposed to the sun, and this is the highest admissible value of ρ_1. In order to keep our investigation as general as possible, I write

$$\rho = \rho_0(1+\gamma'\cos\theta+\gamma\sin\theta\cos\lambda),$$

where γ' and γ may have any assigned values. The solution of our problem is obtained if we can find values of S and R satisfying the equations

$$\left.\begin{aligned} \rho\cot\theta\frac{d\psi}{d\lambda} &= \rho\frac{dS}{d\theta} + \frac{dR}{\sin\theta\, d\lambda} \\ -\rho\cos\theta\frac{d\psi}{d\theta} &= \rho\frac{dS}{\sin\theta\, d\lambda} - \frac{dR}{d\theta} \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (14).$$

R will now give directly the current function which hitherto was denoted by ρ_0R.

The general problem will be treated in the Appendix, where it is shown that for practical purposes γ and γ' may be treated as small quantities, the squares of which may be neglected. The equations may then be written

$$\left.\begin{aligned} \rho \cot \theta \frac{d\psi}{d\lambda} &= \rho_0 \frac{dS}{d\theta} + (1-\gamma' \cos \theta - \gamma \sin \theta \cos \lambda) \frac{dR}{\sin \theta \, d\lambda} \\ -\rho_0 \cos \theta \frac{d\psi}{d\theta} &= \rho_0 \frac{dS}{\sin \theta \, d\lambda} - (1-\gamma' \cos \theta - \gamma \sin \theta \cos \lambda) \frac{dR}{d\theta} \end{aligned}\right\} \quad . \quad . \quad . \quad (15).$$

Neglecting γ and γ', our previous results give R in terms of ψ. Let Q_n^σ be one part of R thus obtained. The next approximation is found by substituting Q_n^σ for R in the terms of (15), which contain γ and γ'.

The complete value of R, as far as it depends on Q_n^σ, will then be $Q_n^\sigma + R'$, where R' is determined by

$$\left.\begin{aligned} (\gamma' \cos \theta + \gamma \sin \theta \cos \lambda) \frac{dQ_n^\sigma}{\sin \theta \, d\lambda} &= \rho_0 \frac{dS'}{d\theta} + \frac{dR'}{\sin \theta \, d\lambda} \\ -(\gamma' \cos \theta + \gamma \sin \theta \cos \lambda) \frac{dQ_n^\sigma}{d\theta} &= \rho_0 \frac{dS'}{\sin \theta \, d\lambda} - \frac{dR'}{d\theta} \end{aligned}\right\} \quad . \quad . \quad . \quad (16).$$

In the two cases which specially interest us we must substitute for Q_n^σ the values respectively of R_2^1 and ρR_3^2 as determined by (5). The solution of (16) involves the elimination of S'.

Treating the terms containing γ and γ' separately, we find for R' as far as it depends on γ',

$$\gamma' \left(\cot \theta \frac{d^2 Q_n^\sigma}{d\lambda^2} + \frac{d}{d\theta} \sin \theta \cos \theta \frac{dQ_n^\sigma}{d\theta} \right) = -\Sigma n \, . \, n+1 \, . \sin \theta \, R'_n,$$

if R' is expressed as a series of harmonics, n being the degree of one of the terms of the series.

The left-hand side may be transformed as shown in the Appendix, the result being given by (25); we obtain in this way

$$\gamma' \left(\frac{(n+2)\, n\, (n-\sigma+1)}{2n+1} Q^\sigma_{n+1} + \frac{(n-1)(n+1)(n+\sigma)}{2n+1} Q^\sigma_{n-1} \right) = \Sigma n \, (n+1) \, R'_n.$$

R' is therefore expressible by two terms, R^σ_{n+1} and R^σ_{n-1}, so that

$$(2n+1)(n+1) \, R^\sigma_{n+1} = \gamma' n \, (n-\sigma+1) \, Q^\sigma_{n+1},$$
$$(2n+1) \, n \, . \, R^\sigma_{n-1} = \gamma' (n+1)(n+\sigma) \, Q^\sigma_{n-1}.$$

As regards the terms in γ, the elimination of S' leads to

$$\gamma \left(\frac{d}{d\lambda} \cos \lambda \frac{d}{d\lambda} + \cos \lambda \frac{d}{d\theta} \sin^2 \theta \frac{d}{d\theta} \right) Q_n^\sigma = -\Sigma n \, (n+1) \sin \theta R'_n.$$

The left-hand side is transformed, as shown in the Appendix, the result being given in (22). We thus find R′ expressible as a sum of four terms—

$$2(2n+1)(n+1)\,\mathrm{R}_{n+1}^{\sigma+1} = \gamma n \mathrm{Q}_{n+1}^{\sigma+1},$$

$$2(2n+1)\,n\,.\,\mathrm{R}_{n-1}^{\sigma+1} = -\gamma(n+1)\,\mathrm{Q}_{n-1}^{\sigma+1},$$

$$2(2n+1)(n+1)\,\mathrm{R}_{n+1}^{\sigma-1} = -\gamma n(n-\sigma+1)(n-\sigma+2)\,\mathrm{Q}_{n+1}^{\sigma-1},$$

$$2(2n+1)\,n(n-1)\,\mathrm{R}_{n-1}^{\sigma-1} = \gamma(n-1)(n+1)(n+\sigma)(n+\sigma-1)\,\mathrm{Q}_{n-1}^{\sigma-1}.$$

For Q_n^σ we must substitute $\frac{1}{6}\mathrm{CA}_1\psi_2^1$ and $\frac{2}{15}\mathrm{CA}_2\psi_3^2$ when treating of the diurnal and semidiurnal variations respectively, where ψ_2^1 and ψ_3^2 are the harmonics of type and degree indicated which have the same factors as the current functions ψ_1^1 and ψ_2^2.

To get the magnetic potential, a further multiplication by $-4\pi(n+1)/2n+1$ is required. We see that each barometric variation now leads to six terms in the magnetic potential, the factors of $-\pi\rho_0 e\mathrm{AC}\Omega_n^\sigma$ being collected in the following table:—

DIURNAL VARIATION.

Velocity Potential : $\mathrm{A}_1\psi_1^1$. Magnetic Potential : $-\pi\rho_0 e\mathrm{A}_1\mathrm{C}\Sigma\mathrm{B}_n^\sigma\Omega_n^\sigma$.

Values of B_n^σ :

	$n = 1.$	$n = 2.$	$n = 3.$
$\sigma = 0$	$\frac{2}{5}\gamma$	—	$-\frac{16}{105}\gamma$
1	$\frac{2}{5}\gamma'$	$\frac{2}{5}$	$\frac{32}{315}\gamma'$
2	—	—	$\frac{8}{315}\gamma$

SEMIDIURNAL VARIATION.

Velocity Potential : $-\pi\rho_0 e\mathrm{A}_2\mathrm{C}\Sigma\mathrm{B}_n^\sigma\Omega_n^\sigma$. Barometric Variation : $\mathrm{A}_2\psi_2^2$.

Values of B_n^σ :—

	$n = 2.$	$n = 3.$	$n = 4.$
$\sigma = 1$	$\frac{64}{105}\gamma$	—	$-\frac{2}{21}\gamma$
2	$\frac{32}{105}\gamma'$	$\frac{32}{105}$	$\frac{4}{63}\gamma'$
3	—	—	$\frac{1}{63}\gamma$

C = Vertical force at geographical North Pole, measured upwards.
ρ_0 = Electric conductivity of atmospheric shell.
e = Thickness of atmospheric shell.

The main terms of the magnetic potentials Ω_2^1 and Ω_3^2 are now each affected by both the diurnal and semidiurnal barometric variation, and their relative amplitudes may differ considerably from those calculated on the assumption of a uniform conductivity. If γ has its maximum value, which is unity, we have for these two terms, neglecting an unimportant difference of phase, and leaving out common factors,

$$\Omega_2^1 = \frac{2}{5}A_1 + \frac{64}{105}A_2 = 21 \cdot 0 \frac{a}{\pi},$$

$$\Omega_3^2 = \frac{32}{105}A_2 + \frac{8}{315}A_1 = 4 \cdot 7 \frac{a}{\pi}.$$

The 24-hourly variation of terrestrial magnetism now takes the lead and as regards westerly force is now 4·7 times as great as the semidiurnal variation, but the latter is still too great for complete agreement with the facts, the observational ratio being 8·8. This remaining discrepancy is not decisive against the accuracy of the assigned cause in view of the uncertainty which attaches to the 24-hourly term in the barometric variation as explained in § 4, and the considerations brought forward in the following paragraph. There is the theoretical possibility of a further increase in the diurnal term through a velocity proportional to P_2^0; the motion specified by this potential would give a barometric oscillation determined by the time of some definite meridian, and though observations seem to indicate the existence of part of the oscillation being of this nature, it is not likely that it is sufficiently great to produce a marked magnetic effect.

12. A general review of the argument, even at the risk of repeating a portion of what has already been said, may be appropriate, and is necessary to show how we are naturally led to the theory here proposed. It will also serve to introduce the consideration of the remaining difficulties and of the possibility of accounting for the amount of ionisation necessary to explain the magnitude of the observed effects.

Our object is to explain the cause of the periodic changes of the terrestrial magnetic forces in so far as they depend on the position of the sun. The diurnal changes may be represented as being governed by a magnetic potential Ω composed of terms of the form $\Omega_n^\sigma \cos \sigma(\lambda + t)$, where Ω_n^σ is a surface harmonic; the observed vertical forces show, as proved in my previous communication, that we must seek the cause of the variation outside the earth's surface. Electric currents circulating in our atmosphere and having a current function made up of terms which are respectively proportional to Ω_n^σ produce the required effect, and we are justified in assuming this—the simplest explanation—to be also the correct one until it is shown to lead to contradictions. The maintenance of the electric currents necessarily requires an electromotive force, and their closed lines of flow dispose of any theory which would seek this force in a static distribution of potential. Electric charges carried along by air currents have been shown to be insufficient to produce appreciable effects, and we are therefore driven to look upon electromagnetic induction as being the only possible cause of the observed effects, the earth's magnetism and atmospheric circulation being the active agents. Assuming as most probable that atmospheric circulation is symmetrical north and south of the equator, the character of the magnetic variation shows that the effective component of terrestrial magnetism has opposite signs in the two hemispheres; it must therefore be the vertical component which is active. We next put the question: What must be the atmospheric circulation which under the action of the vertical magnetic force produces periodical magnetic effects equal to those actually observed? Taking the average for the complete year, the leading terms of the variable magnetic potential are $\Omega_2^1 \cos(\lambda+t)$ and $\Omega_3^2 \cos 2(\lambda+t)$, the amplitude of the diurnal term being equal to about eight times the amplitude of the semidiurnal one. Calculation shows that Ω_2^1 may be produced by a quasi-tidal atmospheric flow having as velocity potential either $\psi_1^1 \cos(\lambda+t)$ or $\psi_3^1 \cos(\lambda+t)$, while the semidiurnal term may be produced by a flow having a velocity potential $\psi_2^2 \cos 2(\lambda+t)$ or $\psi_4^2 \cos 2(\lambda+t)$. But these velocity potentials are exactly what is required for the atmospheric waves causing the daily changes of barometric pressure. The semidiurnal term of the pressure change is the one least affected by local conditions, and its distribution over the earth's surface is therefore accurately known. It is found that ψ_4^2 is small compared with ψ_2^2. As regards the diurnal term having an amplitude at the equator of only one-third of the semidiurnal one, it varies somewhat irregularly and the relative importance of ψ_1^1 and ψ_3^1 is not well ascertained. Assuming the barometric variation to be wholly due to $\psi_1^1 \cos(\lambda+t)$ and $\psi_2^2 \cos 2(\lambda+t)$, we may deduce the magnetic variation and compare it with the observed changes. This has been the course of the investigation in the preceding paragraphs. It is found that the calculated magnetic variations have a phase which lags behind the observed one by about $1\frac{3}{4}$ hours, and this lag is slightly less for the diurnal term, but the difference is insignificant in view of the uncertainties of the data. The amplitude of the calculated diurnal term is about $2\frac{1}{2}$ times as great as that of the semidiurnal one, while observation gives, as has already been stated, a ratio of 8 for the two terms. But if part of the barometric variation is due to a term ψ_3^1—and there is some evidence that this is the case—agreement in the ratio of the two terms may be secured. There is, however, a further cause tending to increase the semidiurnal magnetic variation. In order to explain, on the basis of our theory, the difference in the magnetic changes between summer and winter, we must assume that the conductivity of the atmosphere is greater in that hemisphere which is more directly under the influence of the solar rays. Assuming that the electric conductivity is proportional to $1+\cos\omega$, where ω is the angle measured on the celestial sphere between the sun and the point considered, the calculated semidiurnal term reaches a value which is 4·7 times as great as that of the diurnal term, so that the term ψ_3^1 is now called upon to a much smaller extent for making up the deficiency in the diurnal term. The supposed inequalities of conductivity, though helping towards a better agreement between the diurnal and semidiurnal terms, are insufficient to account completely for the large excess of the summer variation over that observed in winter. This inequality is expressed by Ω_3^2 for the semidiurnal variation and Ω_2^1 for the diurnal variation, and its relative magnitude is indicated by the ratios Ω_3^2/Ω_2^2 and Ω_2^1/Ω_1^1 respectively. The calculated value of both ratios is shown by the tables in § 10 to be $\gamma' = \sin \delta$, where δ is the sun's declination. If we compare the variations during the six summer months with those during the six winter months, we must substitute for $\sin \delta$ its average value, which is about 0·26. On the other hand, the results of my previous communication allow us to deduce the ratios Ω_3^2/Ω_2^2 and Ω_2^1/Ω_1^1 from the observations, and we find in this 0·6 and 0·8 respectively, or values between two and three times as great as those calculated from the assumed law of conductivity.

To explain the difference we might imagine some cumulative effect, so that in midsummer the conduction would be greater than in winter even for the same elevation of the sun, but our present knowledge does not justify us in assuming this to be the case. I am inclined, therefore, to consider that the cause of the discrepancy lies in the fact that, as already suggested in the introductory remarks, the oscillations responsible for the barometric and magnetic phenomena are to some extent independent of each other, affecting different layers of the atmosphere. There are theoretical reasons why this should be so. It is now, I think, generally recognised that the importance of the semidiurnal variation of the barometer is due to the fact that the free period of the atmospheric oscillation, dependent on the velocity potential ψ_2^2, is very nearly equal to 12 hours. But it is to be remarked that if concentric layers of the atmosphere be considered separately, there must be a considerable variation in the free periods owing to differences of temperature, and in the highest regions, in which alone electric currents of sufficient intensity can circulate, the temperature is probably so low that the free periods would be more than doubled. If we take these highest layers to oscillate to some extent independently, we should not therefore find the semidiurnal variation stand out in the same way as it does for the lower layers. Further, the inequalities of solar radiation in the two hemispheres near solstice ought to cause an appreciable oscillation dependent on the velocity potentials ψ'_2 and ψ_3^2. The barometric variation due to ψ_3^2 is unimportant compared with that due to ψ_2^2, because although the *forced* period is 12 hours, the free period corresponding to the motion involved in it has now a different value; but in the upper layers the relative importance of ψ_3^2 would be increased, or, as it would be more correct to say, the relative importance of ψ_2^2 disappears. This would account for the magnitude of the seasonal term in the magnetic variation.

The suggested partial independence of the oscillations of the upper and lower atmospheres may also explain the discrepancy of phase, which we found to be $1\frac{3}{4}$ hours, but is in reality somewhat greater, owing to the fact that self-induction has been neglected in calculating the phase. With the calculated conductivity, self-induction would cause a retardation of about one hour if the amplitude of oscillation is that deduced from the barometric variation. If the amplitude in the conducting regions is greater, the effect of self-induction is correspondingly less, because a smaller conductivity would then be required to account for the magnetic change.

A few words should be said on the uncertainties of the data which serve as a test of the proposed theory and which are derived from my previous calculation of the variation potential. In deducing that potential I was practically obliged to confine myself to the records of four observatories (Bombay, Lisbon, Greenwich, St. Petersburg), all four being situated in the northern hemisphere; and the year 1870 being the only one for which records were available at all four stations, I had to base my calculations on the figures for that year. Unfortunately, 1870 was a year of unusual sunspot activity and the magnetic records for that year cannot be taken as quite normal. It is probable that if the average of a number of years were taken, the phases of the components and their relative amplitudes might be somewhat altered; but I do not think that, as far as the averages for the whole year are concerned, the results of the present investigation would be materially altered. A renewed discussion is, however, very desirable, especially if observations in the southern hemisphere could be made use of. In my previous calculations I separated the summer from the winter months, and assuming what is known to be approximately the case, each hemisphere to behave alike when the sun occupies corresponding positions, I was enabled to form an expression of the potential applicable for the whole world simultaneously. But this is admittedly a defective process, and in drawing the equipotential curves I was careful for this reason to use only the averages taken over the whole year and to make no attempt to separate the two hemispheres. VON BEZOLD, who later, basing his calculations on my figures, effected this separation, is often quoted as having thus completed my own investigation, but his extension of my work, for the reason given, seems to me to be deceptive and to push too far the observed approximate symmetry in the two hemispheres. What I now regret, however, is that I did not divide the year into four parts instead of two, as Dr. CHREE'S results seem to show that the time of equinoxes deserves special consideration.

If the views here brought forward are correct, all peculiarities of the barometric variation should be reproduced in the magnetic effect, though we must remember that the converse does not hold, and that peculiarities of the magnetic effect depending partly on variations of electric conductivity need have no counterpart in the barometric changes. Thus the greater amplitude of the magnetic variation between summer and winter has already been ascribed to increased conductivity of the atmosphere during the summer. The close relationship between the two phenomena is confirmed by the increased amplitude observed in both near the time of equinoxes. The diurnal period of barometric pressure is known to have maxima at these epochs, and the valuable researches of Dr. CHREE have shown that these maxima are also found in the diurnal variation of the magnetic element. If we take the variation of declination as characteristic, Dr. CHREE'S formula for the semidiurnal term, leaving out the annual variation, is :

$$\delta D = 1{\cdot}82\,[1+0{\cdot}137 \sin (2t+271^\circ)],$$

where t is measured from the beginning of January and each month counts as 30 degrees. The corresponding term in the barometric formula is, according to HANN,*

$$\delta p = 0{\cdot}988\,[1+0{\cdot}061 \sin (2t+293{\cdot}4)],$$

but if I understand the formula correctly, the time here is counted from the middle of January. To make the equations correspond, we must therefore diminish the angle in the last equation by 30 degrees, reducing it to 263·4 degrees, in close agreement with that given by CHREE, the phase angle for the equinox being 265 degrees. The maxima of horizontal force occur, however, a fortnight later, so that too much value should not be given to this agreement ; the effect in amplitude is only about half for the barometric variation ; but questions of conductivity may affect this ratio.

A remarkable feature distinguishing the barometric change is the maximum which takes place simultaneously in both hemispheres early in January when the earth is in perihelion. According to the theory here discussed, a corresponding annual inequality should show itself in the magnetic variation, though the effect would be partially masked in the northern hemisphere by the changes of conductivity, and could only be ascertained by a comparison of the annual terms in the two hemispheres. We should expect the difference between winter and summer to be more marked in the southern hemisphere, because there the effects of conductivity would act in the same direction as the effects of diminished distance from the sun. It is much to be desired that some systematic attempt should be made to investigate the lunar influence on the magnetic changes, for we possess at present only the vaguest information as to how the different components of magnetic force are affected. It is quite possible that the effects may depend on a tidal disturbance of the upper regions of the atmosphere. If so, we may expect to get a valuable test of our theory by their investigation.

13. We are now prepared to discuss the magnitude of the conductivity required in order that the proposed theory should be tenable. If equations (9) and (10) are compared with each other, and the correction discussed in § 5 be applied, we find from the semi-diurnal term

$$\rho e = 3 \times 10^{-6}.$$

The first question which arises is the value to be assigned to e. Observations of the aurora borealis conducted by the Danish expedition under the late Mr. PAULSEN have led to the conclusion that the arc of these luminosities is generally at a height

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* 'Met. Zeitschrift,' 1898, vol. XV., p. 381.

of 400 kilometres.[*] The height of meteors when they become luminous is as a rule over 100 kilometres, but there is one case on record in which a height of 780 kilometres was found. We may therefore take 300 kilometres as an outside limit for e, giving the value of 10^{-13} as the lower limit for the conductivity. This no doubt is a high value, and there may be some hesitation in accepting it as a possible one. Mr. C. T. R. WILSON has, however, already drawn attention to the fact that at high altitudes we must, with the same ionising power, expect a much increased conductivity, for the ionic velocity due to unit difference of potential varies inversely with the pressure. If, further, as the experiments indicate, the ionising power and rate of recombination of ions both diminish directly as the pressure, it would follow that when the pressure is only the millionth part of an atmosphere the conductivity should be for the same ionisation a million times as great as at the surface of the earth.

Researches on the conductivity of gases generally give relative measures, so that it is not always easy to infer its value in C.G.S. units, but I think the following examples will give an idea of the order of magnitude involved.

The quantity of electricity in the form of ions of each kind under normal conditions at the surface of the earth is $0{\cdot}33 \times 10^{-16}$ in electromagnetic measure. To obtain the conductivity the figures must be multiplied by the ionic velocity per unit fall of potential, the sum of the velocities of both kinds of ions being 3×10^{-8}. The conductivity of air at the surface of the earth is therefore under normal conditions 10^{-24}. GERDIEN, in one of his balloon ascents, determined the conductivity at a height of 6000 metres and found it to be 2×10^{-24}, which, as far as it goes, confirms the conclusion that the conductivity is inversely proportional to the density. At a height such that the pressure is one dyne per square centimetre, and assuming that the recombination of ions is not materially affected by the low temperature, we should thus get a conductivity of 10^{-18}, showing that, if the views discussed in this paper are correct, the ionising power at great altitudes must be considerably greater than that which acts on the air near the surface of the earth.

In speaking of the ionising effects of Röntgen rays, Professor J. J. THOMSON[†] states that even when the ionisation is exceptionally large the proportion of the number of free ions to the number of molecules of the gas is less than 1 to 10^{12}. From this I calculate the conductivity to be about 10^{-20} at atmospheric pressure. Some experiments by RUTHERFORD fix the conductivity of air, subject to the action of radium having an activity 1000 times less than pure radium, to be $0{\cdot}7 \times 10^{-19}$ under normal conditions. These figures would give to the conductivity of air at a pressure equal to that of a millionth atmosphere a magnitude comparable with that required. We know of much more powerful ionisers than the Röntgen tube or even radium. An electric discharge itself is sufficient to ionise a gas, as I proved as far back as

[*] 'Rapports du Congrès International de Physique,' vol. III., p. 438 (1900).

[†] 'Conductivity of Electricity through Gases,' p. 256.

1887. Data supplied by H. A. WILSON* show that in the positive column of a vacuum tube the conductivity reaches the value 10^{-13} and the kathode glow is even more highly conducting. The same author has experimented with air ionised in contact with hot platinum, and the data supplied by his diagrams† allow us to fix the conductivity of such air as about 4×10^{-17} at a temperature of 1080°. When the air was charged with the spray from a 1 per cent. solution of a potassium salt, the conductivity rose to $1 \cdot 4 \times 10^{-13}$, the temperature being 1200°. The conductivity of a Bunsen burner has been measured by GOLD and found to be 8×10^{-15}. In view of these figures, which all apply of course to atmospheric pressure, we ought not, I think, to reject the value of 10^{-13} as an impossible one for the conductivity of air at high altitudes, but it is necessary to inquire into causes which produce so strong an ionisation.

The increased intensity of the magnetic variation during the summer months suggests directly that we are dealing with a solar action. This action may be simply an effect of radiation or it may be due to an injection of ions into the atmosphere. The former hypothesis is the one which presents itself as the most natural one, though the coronal streamers lend some countenance to the second view, which has often been put forward and sometimes even pressed in support of wildly speculative theories.

Ultra-violet radiation is known to ionise air in contact with metallic surfaces, but the evidence is somewhat conflicting as to the effect of radiation on the air itself. Unless the air is absolutely free of dust, the observed action may be due to the illumination of the dust and not of the air. Dust-free air is so transparent to luminous radiation that it would not be surprising if the ionising effect would disappear, as some experimenters believe it to do, when proper precautions are taken. On the other hand, Dr. V. SCHUMANN has shown that air has a very strong absorbing power for wave-lengths which are sufficiently short. Such short wave-lengths are supplied by several metallic sparks, and are freely transmitted through hydrogen. Nevertheless it seems difficult to believe that, even if emitted by the hottest portion of the sun's envelope, they are not absorbed again by the surrounding cooler layers. We are not, therefore, at present in a position to assert that sufficiently short wave-lengths can enter the atmosphere and be absorbed in the outer layer, thereby causing ionisation, but we know so little about the conditions of the uppermost layers that we may reasonably retain the view that the powerful ionisation of the air, which we must consider to be an established fact, is a direct effect of solar radiation.

If we turn to the possibility of a direct injection of ions by the sun into our atmosphere, we have to deal with the alternatives of supposing that ions of both kinds are introduced or only those of one kind. The second alternative must be rejected at once, because a simple calculation shows that the outward force due to the volume

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* 'Phil. Mag.,' 1900, p. 512.

† 'Phil. Trans.,' vol. 202, p. 243 (1904).

electrification of air necessary to account for the required conductivity would be more than sufficient to overcome gravitation and to drive out the conducting portions at an enormous rate. The injection, on the other hand, of a sufficient number of ions of both kinds also presents difficulties on account of the large quantity of new matter which would have to accumulate in our air, especially if it is considered that recombination at a rapid rate would take place both in the journey from the sun to the earth and in the passage through the different layers of the atmosphere. The only alternative to ultra-violet radiation seems, therefore, to lie in the injection of ions travelling with sufficient rapidity to generate other ions by impact. The air itself, according to this view, would supply the raw material for the ionisation, the injected corpuscles only acting as fertilisers. There are, of course, other possibilities, such as the introduction of radioactive matter, or a spontaneous ionisation which may, if the rate of recombination is slow, be very effective at a great height; but that the sun undoubtedly plays an important part in the process is shown not only by the summer effect, but also by the periodic changes of the magnetic variation, which corresponds with the sunspot cycle. I have held for many years and frequently expressed the opinion that the relationship can only be explained satisfactorily on the supposition that the electric conductivity at times of many sunspots is increased. Whether this is a direct influence of the sun, or only an indication that an ionising influence is brought into the solar system from outside at times of many sunspots, is a question which everyone is likely to answer according to his individual views of the cause of sunspot variability.

That the increase in the number of sunspots coincides with an increased conductivity of the upper layers of the atmosphere is also indicated by the eleven years' period of the aurora borealis. The distinguishing feature of the relationship seems to be this, that auroral displays extend further into moderate latitudes when the solar activity is great. An increase of conductivity is the simplest and most natural way of accounting for the effect. The primary cause of the electric discharges which manifest themselves in the aurora is still unknown. We may look for it, perhaps, in electrostatic forces which are always present, but causing a visible discharge only when their intensity rises abnormally, the course and intensity of discharge being much affected by inequalities of conducting power. On the other hand, there are other electromotive forces of induction not discussed in the paper, such as those accompanying a general drift of the atmosphere from west to east, which may well have something to do with the cause of auroral displays. Or again, if interplanetary space contains sufficient matter to be conducting, as I believe it must, there will be strong electromotive forces acting in the earth's magnetic field between the conducting powers rotating with the earth and those of interplanetary space.

Outbreaks of magnetic disturbances, affecting sometimes the whole of the earth simultaneously, may be explained by sudden local changes of conductivity which may extend through restricted or extensive portions of the atmosphere. I have shown in another place that the energy involved in a great magnetic storm is so considerable that we can only think of the earth's rotational energy as the source from which it ultimately is drawn. The earth can only act through its magnetisation in combination with the circulation of the atmosphere, so that magnetic storms may be considered to be only highly magnified and sudden changes in the intensity of electric currents circulating under the action of electric forces which are always present.

Those currents only are discussed in this communication which produce periodic variations in the magnetic elements, but there are also electromotive forces giving rise to current functions which are expressed by zonal harmonics and cannot under ordinary circumstances be observed, though any variation of conductivity between summer and winter would produce an annual period.

One further consequence of the theory deserves to be noticed. The electric currents indicated by our theory are sufficiently large to produce a sensible heating effect in the low-pressure regions through which they circulate. They will protect, therefore, the outer sheets of the atmosphere from falling to the extremely low temperatures which sometimes have been assumed to exist there, and they may help to form the isothermal layer which balloon observations have proved to exist at a height of about 50,000 feet.

Enough has been said to show the importance of the questions on which further investigation of the diurnal variation must give valuable information. If the fundamental ideas underlying the present enquiry stand the test of further research, we are in possession of a powerful method which will enable us to trace the cosmical causes which affect the ionisation of the upper regions of the atmosphere and which act apparently in sympathy with periodic effects showing themselves on and near the surface of the sun. It should be our endeavour to put the theory itself to a more accurate test than can at present be done. The most promising line of attack seems to me to be the investigation of the diurnal variation near the equator, where, as explained in § 6, it should not only vary with local time, but possess a term depending on the time of the meridian which passes through the magnetic axis. An exact determination of lunar effects would also, as has already been pointed out, serve as a valuable test of the theory.

PART II.

The problem to be solved may be stated thus: a spherical shell of fluid is animated by a quasi-tidal motion and is under the influence of magnetic forces of which only the vertical components are considered. It is required to find the magnetic effect of the induced currents if the motion is subject to a velocity potential $\psi_n^\sigma \cos \sigma (\lambda+t-\alpha)$, where ψ_n^σ is a surface harmonic, λ the longitude measured from some standard meridian towards the east, and t is the local time of that meridian. The conductivity ρ of the fluid is not necessarily uniform, but we take it to be expressible in the form

$$\rho = \rho_0+\rho_1 \cos \theta+\rho_2 \sin \theta \cos (\lambda+t),$$

where θ is the colatitude, and $\lambda+t$ measures the difference in longitude between the sun and the place at which ρ is required. The question is solved if we can determine the current function of the electric currents which are generated by the fluid moving through the magnetic field. The problem for constant conductivity has been treated in the first part of this communication and the interest of a non-uniform conducting power is confined to the case that the variability depends on the angular distance between the sun and the point considered. If ω be this angle, the effect of the sun's radiation will be proportional to $\cos\omega$ in the hemisphere subject to the radiation, *i.e.* for values of ω smaller than $\frac{1}{2}\pi$. If the induction is due to the ionising power of the sun's rays, the rate of recombination of ions has to be considered, but unless this rate is of a different order of magnitude from that observed near the surface of the earth, the conductivity may be considered to be proportional everywhere to the illuminating power. For values of ω intermediate between $\frac{1}{2}\pi$ and π we must, then, give zero value to the conductivity. By means of Fourier series we may now express the conductivity in a series

$$\rho = \rho'_0\left[\frac{2}{\pi}+\tfrac{1}{2}\cos\omega+\frac{2}{3\pi}\cos 2\omega+\ldots\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17),$$

which satisfies the condition

$$\rho = \rho'_0\cos\omega \text{ for } 0<\omega<\frac{\pi}{2}, \quad\text{and}\quad \rho=0 \text{ for } \frac{\pi}{2}<\omega<\pi.$$

Confining ourselves to the first two terms and substituting the value of $\cos\omega$ from (13) in terms of the hour-angle of the sun and its declination, we obtain

$$\rho = \rho'_0\left[\frac{2}{\pi}+\tfrac{1}{2}\sin\delta\cos\theta+\tfrac{1}{2}\cos\delta\sin\theta\cos(\lambda+t)\right].$$

The conductivity has therefore the assumed form if we put

$$\rho_0 = \frac{2}{\pi}\rho'_0; \quad \rho_1 = \tfrac{1}{2}\rho'_0\sin\delta; \quad \rho_2 = \tfrac{1}{2}\rho'_0\cos\delta.$$

Were we to adopt the simpler form and put the conductivity proportional to $1+\cos\omega$, so that it reaches zero value only at midnight, we should have to put

$$\rho_1 = \rho_0\sin\delta; \quad \rho_2 = \rho_0\cos\delta,$$

and in every case ρ can be expressed in terms of a series such as (17), our investigation by proper adjustment of the constants taking account of the first two terms. The term in $\cos 2\omega$ might be taken into consideration without much difficulty should that become necessary. The value of ρ_0 can provisionally be put equal to unity and re-introduced at a later stage. Writing $\gamma' = \rho_1/\rho_0$ and $\gamma = \rho_2/\rho_0$ we may therefore put

$$\rho = 1+\gamma'\cos\theta+\gamma\sin\theta\cos(\lambda+t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18).$$

In order to avoid frequent interruption, I prove in the first instance a few formulæ of transformation which I have found of great utility in these investigations. I start from the following equations denoted in my previous communications by Roman letters, which it is convenient to retain :

$$(2n+1)\cos\theta Q_n^\sigma = (n-\sigma+1)\, Q^\sigma{}_{n+1} + (n+\sigma)\, Q^\sigma{}_{n-1} \quad \ldots \quad (\mathrm{A}),$$

$$(2n+1)\sin\theta Q_n^\sigma = Q_{n+1}{}^{\sigma+1} - Q_{n-1}{}^{\sigma+1} \quad \ldots \quad (\mathrm{B}),$$

$$= (n+\sigma)(n+\sigma-1)\, Q_{n-1}{}^{\sigma-1} - (n-\sigma+2)(n-\sigma+1)\, Q_{n+1}{}^{\sigma-1} \quad . \quad (\mathrm{C}),$$

$$\frac{2\sigma Q_n^\sigma}{\sin\theta} = (n+\sigma)(n+\sigma-1)\, Q_{n-1}{}^{\sigma-1} + Q_{n-1}{}^{\sigma+1} \quad \ldots \quad (\mathrm{D}),$$

$$= Q_{n+1}{}^{\sigma+1} + (n-\sigma+2)(n-\sigma+1)\, Q_{n+1}{}^{\sigma-1} \quad \ldots \quad (\mathrm{E}),$$

$$\frac{2dQ_n^\sigma}{d\theta} = (n+\sigma)(n-\sigma+1)\, Q_n{}^{\sigma-1} - Q_n{}^{\sigma+1} \quad \ldots \quad (\mathrm{H}_1).$$

Q_n^σ denotes the tesseral function derived from the zonal harmonic P_n by the relation $Q_n^\sigma = \sin^\sigma.\theta \dfrac{d^\sigma P_n}{d\mu^\sigma}$, where $\mu = \cos\theta$.

Multiplying (D) by $(n-\sigma+1)$ and (E) by $(n+\sigma)$, and adding, we find, with the help of (A),

$$(2n+1)\left[(n+\sigma)(n-\sigma+1)\cos\theta Q_n^{\sigma-1} - \frac{2\sigma}{\sin\theta} Q_n^\sigma\right] = -(n+\sigma)\, Q_{n+1}{}^{\sigma+1} - (n-\sigma+1)\, Q_{n-1}{}^{\sigma+1}.$$

If in the formula (A) we substitute $\sigma+1$ for σ, it becomes

$$(2n+1)\cos\theta Q_n^{\sigma+1} = (n-\sigma)\, Q_{n+1}{}^{\sigma+1} + (n+\sigma+1)\, Q_{n-1}{}^{\sigma+1}.$$

From the last two equations we obtain, by subtraction and substitution of (H_1),

$$(2n+1)\cos\theta \frac{dQ_n^\sigma}{d\theta} - \frac{\sigma}{\sin\theta} Q_n^\sigma = -nQ_{n+1}{}^{\sigma+1} - (n+1)\, Q_{n-1}{}^{\sigma+1}.$$

Now multiplying (B) by $n\,.\,(n+1)$, and subtracting, we finally obtain

$$\sin\theta\cos\theta \frac{dQ_n^\sigma}{d\theta} - n\,.\,n+1\,.\sin^2\theta Q_n^\sigma - \sigma Q_n^\sigma$$
$$= \sin\theta \frac{(n-1)(n+1)\, Q_{n-1}{}^{\sigma+1} - n(n+2) Q_{n+1}{}^{\sigma+1}}{2n+1} \quad . \quad . \quad (\mathrm{K}_1).$$

If on the right-hand side of (K_1) we substitute the values of $Q_{n+1}{}^{\sigma+1}$ and $Q_{n-1}{}^{\sigma+1}$ from D and E, we obtain a corresponding equation

$$\sin\theta\cos\theta \frac{dQ_n^\sigma}{d\theta} - n\,.\,n+1\,.\sin^2\theta\,.\,Q_n^\sigma + \sigma Q_n^\sigma$$
$$= \frac{\sin\theta}{2n+1}\left\{n(n+2)(n-\sigma+2)(n-\sigma+1) Q_{n+1}{}^{\sigma-1} - (n-1)(n+1)(n+\sigma)(n+\sigma-1)\, Q_{n-1}{}^{\sigma-1}\right\}$$
$$. \quad . \quad . \quad (\mathrm{K}_2).$$

A further useful transformation is derived from the equations

$$(2n+1)\,\sigma\cos\theta Q_n^{\sigma} = \sigma\,(n-\sigma+1)\,Q^{\sigma}{}_{n+1}+\sigma\,(n+\sigma)\,Q^{\sigma}{}_{n-1},$$

$$(2n+1)\sin\theta\frac{dQ_n^{\sigma}}{d\theta} = n\,.\,(n-\sigma+1)\,Q^{\sigma}{}_{n+1}-(n+1)\,(n+\sigma)\,Q^{\sigma}{}_{n-1}.$$

If we subtract and add these equations, they reduce to

$$\sigma\cos\theta Q_n^{\sigma}-\sin\theta\frac{dQ_n^{\sigma}}{d\theta} = \sin\theta Q_n^{\sigma+1} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (\mathrm{L}_1),$$

and

$$\sigma\cos\theta Q_n^{\sigma}+\sin\theta\frac{dQ_n^{\sigma}}{d\theta} = (n+\sigma)\,(n-\sigma+1)\sin\theta Q_n^{\sigma-1} \quad . \; . \; . \; . \quad (\mathrm{L}_2).$$

We shall require to find the effect of the operation

$$\left(\frac{d}{d\lambda}\cos\lambda\frac{d}{d\lambda}+\cos\lambda\frac{d}{d\theta}\sin^2\theta\frac{d}{d\theta}\right)Q_n^{\sigma}\cos(\sigma\lambda-\alpha) \quad . \; . \; . \; . \quad (19).$$

We omit, for the sake of shortness, temporarily the constant α, and divide the operation into two parts, the first being

$$\cos\lambda\left(\frac{d^2}{d\lambda^2}+\sin\theta\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\right)Q_n^{\sigma}\cos\sigma\lambda.$$

From the fundamental equation relating to tesseral harmonics this is equal to

$$-\tfrac{1}{2}n\,.\,(n+1)\sin^2\theta Q_n^{\sigma}\left[\cos(\sigma+1)\lambda+\cos(\sigma-1)\lambda\right] \quad . \; . \; . \; . \quad (20).$$

The remaining part of the operation is

$$\sigma\sin\lambda\sin\sigma\lambda Q_n^{\sigma}+\sin\theta\cos\theta\cos\lambda\cos\sigma\lambda\frac{d}{d\theta}Q_n^{\sigma}$$

$$= \tfrac{1}{2}\cos(\sigma+1)\lambda\,(\sin\theta\cos\theta\, dQ_n^{\sigma}-\sigma Q_n^{\sigma})+\tfrac{1}{2}\cos(\sigma-1)\lambda\,\left(\sin\theta\cos\theta\frac{dQ_n^{\sigma}}{d\theta}+\sigma Q_n^{\sigma}\right) \;.\; (21).$$

If (20) and (21) are now added, and K_1 and K_2 are applied, we find the result of the operation to be, restoring α,

$$\frac{\sin\theta}{2\,.\,2n+1}\left\{(n-1)\,(n+1)\,Q_{n-1}^{\sigma+1}-n\,.\,n+2\,.\,Q_{n+1}^{\sigma+1}\right\}\cos\left\{(\sigma+1)\,\lambda-\alpha\right\}$$

$$+\frac{\sin\theta}{2\,.\,2n+1}\left\{n\,(n+2)(n-\sigma+2)(n-\sigma+1)Q_{n+1}^{\sigma-1}-(n-1)(n+1)(n+\sigma)(n+\sigma-1)Q_{n-1}^{\sigma-1}\right\}$$

$$\cos\left\{(\sigma-1)\,\lambda-\alpha\right\} \quad . \; . \; . \quad (22).$$

We may note that each of the equations used, and therefore the final results, remains true for $\sigma = 0$, if we define

$$n\,.\,n+1\,.\,Q_n^{-1} = -Q'_n.$$

This is in agreement with RODRIGUEZ's theorem, if the definition of Q_n^{σ} depending on the operation

$$(1-\mu^2)^{\frac{\sigma}{2}} d^{n+\sigma} (\mu^2-1)^n / 2^n n! \, d\mu^{n+\sigma}$$

is extended to negative values of σ, for in that case

$$\begin{aligned} Q_n^{-\sigma} &= \frac{1}{2^n n!} (1-\mu^2)^{-\frac{\sigma}{2}} \frac{d^{(n-\sigma)} (\mu^2-1)^n}{d\mu^{n-\sigma}} \\ &= (-1)^{\sigma} \frac{1}{2^n n!} \frac{(n-\sigma)!}{(n+\sigma)!} \frac{d^{n+\sigma} (\mu^2-1)^n}{d\mu^{n+\sigma}} \\ &= (-1)^{\sigma} \frac{(n-\sigma)!}{(n+\sigma)!} Q_n^{\sigma} \quad \ldots \ldots \ldots \ldots (23). \end{aligned}$$

It follows that the operation (17), in the case where $Q_n^0 \cos \alpha$ replaces $Q_n^{\sigma} \cos (\sigma\lambda - \alpha)$, reduces to

$$\frac{\sin \theta}{2 \,.\, 2n+1} \{(n-1)(n+1) Q'_{n-1} - n(n+2) Q'_{n+1}\} [\cos (\lambda - \alpha) + \cos (\lambda + \alpha)].$$

This result may also easily be obtained independently, but in view of the ultimate application of (22) it is important to include the special case in the general one.

It will be appropriate here to obtain another formula which will be used subsequently. Let it be required to find

$$\cot \theta \frac{d^2 Q_n^{\sigma}}{d\lambda^2} + \frac{d}{d\theta} \sin \theta \cos \theta \frac{dQ_n^{\sigma}}{d\theta} \quad \ldots \ldots \ldots \quad (24).$$

From the fundamental equation we find this to be equal to

$$-n \,.\, n+1 \,.\, \sin \theta \cos \theta Q_n^{\sigma} - \sin^2 \theta \frac{dQ_n^{\sigma}}{d\theta},$$

and as

$$-n \,.\, n+1 \,.\, \cos \theta Q_n^{\sigma} = -\frac{n \,.\, n+1}{2n+1} \{(n+\sigma) Q^{\sigma}_{n+1} + (n-\sigma+1) Q^{\sigma}_{n+1}\}$$

and

$$-\sin \theta \frac{dQ_n^{\sigma}}{d\theta} = \frac{1}{2n+1} \{(n+1)(n+\sigma) Q^{\sigma}_{n-1} - n(n-\sigma+1) Q^{\sigma}_{n+1}\},$$

(24) becomes equal to

$$-\frac{\sin \theta}{2n+1} \{(n+2) n (n-\sigma+1) Q^{\sigma}_{n+1} + (n-1)(n+1)(n+\sigma) Q^{\sigma}_{n-1}\} \quad . \ . \quad (25).$$

We are now in a position to attack our main problem. The equations to be solved are

$$\rho X = \rho \frac{dS}{d\theta} + \frac{dR}{\sin \theta \, d\lambda}, \quad \rho Y = \rho \frac{dS}{\sin \theta \, d\lambda} - \frac{dR}{d\theta} \quad \ldots \ldots \quad (14),$$

where X and Y have the values given in (1), and for ρ we must substitute the expression (18), remembering, however, that we must ultimately restore the factor ρ_0. We may also temporarily omit the factor C in the expression for the electric forces. To find the current function R we must eliminate S, but owing to the fact that ρ contains θ and λ, this does not seem to be possible directly. The difficulty must be turned by eliminating in the first place R, and if S is then found, R may be determined from the first of the above equations. It may occur to the reader that R might be more directly obtained if the resistivity were introduced instead of the conductivity. This is true, but the results are less valuable, as may be seen from the fact that, as suggested above, the Fourier expansion may have to be applied to the conducting power in so far as it depends on the position of the sun. If the resistivity were introduced as the variable, the high and possibly infinite values which the factor would take when the conductivity sinks low or vanishes would present difficulties much greater than those met with by keeping the conductivity as the variable quantity.

The elimination of R requires in the first instance the reduction of

$$\frac{d}{d\theta}\rho\mathrm{X}\sin\theta+\frac{d}{d\lambda}\rho\mathrm{Y},$$

i.e. of

$$\rho\left(\frac{d}{d\theta}\mathrm{X}\sin\theta+\frac{d}{d\lambda}\mathrm{Y}\right)+\mathrm{X}\sin\theta\frac{d\rho}{d\theta}+\mathrm{Y}\frac{d\rho}{d\lambda}.$$

Introducing the values of X and Y, the operation reduces to

$$-(1+\gamma'\cos\theta+\gamma\sin\theta\cos\lambda)\sin\theta\frac{d\psi}{d\lambda}-\gamma'\sin\theta\cos\theta\frac{d\psi}{d\lambda}$$
$$-\gamma\cos\theta\left(\cos\theta\cos\lambda\frac{d\psi}{d\lambda}-\sin\theta\sin\lambda\frac{d\psi}{d\theta}\right).$$

The part independent of γ and γ' is

$$-\sin\theta\frac{d\psi}{d\lambda}=-\sigma\sin\theta\psi_n{}^\sigma\cos(\sigma\lambda-\alpha).$$

The part depending on γ' is

$$-2\gamma'\sin\theta\cos\theta\frac{d\psi}{d\lambda}=-2\gamma'\sigma\sin\theta\cos\theta\psi_n{}^\sigma\cos(\sigma\lambda-\alpha)$$
$$=-2\gamma'\sigma\sin\theta\frac{(n-\sigma+1)\psi^\sigma{}_{n+1}+(n+\sigma)\psi^\sigma{}_{n-1}}{2n+1}.$$

We are left with the part dependent on γ, the factor of which is

$$\cos\lambda\frac{d\psi}{d\lambda}(\cos^2\theta-\sin^2\theta)+\sin\theta\cos\theta\sin\lambda\frac{d\psi}{d\theta}.$$

Of this we take separately

$$- \sin^2\theta \cos\lambda \frac{d\psi}{d\lambda}$$

$$= - \frac{\sin^2\theta}{2} [\cos\{(\sigma+1)\lambda-\alpha\} + \cos\{(\sigma-1)\lambda-\alpha\}]\,\psi_n{}^\sigma$$

$$= - \sigma \sin\theta \frac{\psi_{n+1}{}^{\sigma+1} - \psi_{n-1}{}^{\sigma+1}}{2\,.\,2n+1} \cos\{(\sigma+1)\lambda-\alpha\}$$

$$= - \sigma \sin\theta \frac{(n+\sigma)(n+\sigma-1)\psi_{n-1}{}^{\sigma-1} - (n-\sigma+2)(n-\sigma+1)\psi_{n+1}{}^{\sigma-1}}{2\,.\,2n+1} \cos\{(\sigma-1)\lambda-\alpha\}.$$

The remaining terms depending on γ are

$$\tfrac{1}{2} \frac{\cos\theta}{2n+1} \Big[\sigma \cos\theta \psi_n{}^\sigma (\cos\{(\sigma+1)\lambda-\alpha\} + \cos\{(\sigma-1)\lambda-\alpha\})$$
$$+ \sin\theta \frac{d\psi_n{}^\sigma}{d\theta} (\cos\{(\sigma-1)\lambda-\alpha\} - \cos\{(\sigma+1)\lambda-\alpha\}) \Big],$$

or, making use of (L_1) and (L_2),

$$\tfrac{1}{2} \frac{\cos\theta \sin\theta}{2n+1} \psi_n{}^{\sigma+1} \cos[(\sigma+1)\lambda-\alpha] + (n+\sigma)(n-\sigma+1)\,\psi_n{}^{\sigma-1} \cos[(\sigma-1)\lambda-\alpha].$$

The terms containing γ, leaving out the longitude factors, are therefore

$$\frac{\gamma \sin\theta}{2\,.\,2n+1} [(n-2\sigma)\,\psi_{n+1}{}^{\sigma+1} + (n+2\sigma+1)\,\psi_{n-1}{}^{\sigma+1} + (n-\sigma+1)(n-\sigma+2)(n+2\sigma)\,\psi_{n+1}{}^{\sigma-1}$$
$$+ (n+\sigma)(n+\sigma-1)(n-2\sigma+1)\,\psi_{n-1}{}^{\sigma-1}].$$

Collecting our results together, we find as the effect of the operation, eliminating R on the left-hand side of equations (14),

$$\gamma \sin\theta \frac{(n-\sigma+1)(n-\sigma+2)(n+2\sigma)\,\psi_{n+1}{}^{\sigma-1} + (n+\sigma)(n+\sigma-1)(n-2\sigma+1)\,\psi_{n-1}{}^{\sigma-1}}{2\,.\,2n+1}$$
$$\cos\{(\sigma-1)\lambda-\alpha\}$$
$$-\sigma \sin\theta \left[\psi_n{}^\sigma + 2\gamma' \frac{(n-\sigma+1)\,\psi^\sigma{}_{n+1} + (n+\sigma)\,\psi^\sigma{}_{n-1}}{2n+1} \right] \cos(\sigma\lambda-\alpha)$$
$$+\gamma \sin\theta \frac{(n-2\sigma)\,\psi_{n+1}{}^{\sigma+1} + (n+2\sigma+1)\,\psi_{n-1}{}^{\sigma+1}}{2\,.\,2n+1} \cos\{(\sigma+1)\lambda-\alpha\} \quad . \quad . \quad . \quad . \quad . \quad (26).$$

The expression reduces to about half its terms when $n = \sigma$, and for the two special cases which form the main subject of the present inquiry we have then

Case I. $n = 1$, $\sigma = 1$.

$$\frac{1}{\sin\theta} \left(\frac{dP\rho \sin\theta}{d\theta} + \frac{dQ\rho}{d\lambda} \right) = \gamma \psi_2{}^0 \cos\alpha - (\psi_1{}^1 + \tfrac{2}{3}\gamma'\psi_2{}^1) \cos(\lambda-\alpha) - \tfrac{1}{6}\gamma\psi_2{}^2 \cos(2\lambda-\alpha).$$

Case II. $n = 2$, $\sigma = 2$.

$$\frac{1}{\sin\theta}\frac{d\mathrm{P}\rho\sin\theta}{d\theta} + \frac{d\mathrm{Q}\rho}{d\lambda} = \tfrac{6}{5}\gamma\left(-\psi_1{}^1+\psi_3{}^1\right)\cos\left(\lambda-\alpha\right) - \left(2\psi_2{}^2+\tfrac{4}{5}\gamma'\psi_3{}^2\right)\cos\left(2\lambda-\alpha\right)$$
$$-\tfrac{1}{5}\gamma\psi_3{}^3\cos\left(3\lambda-\alpha\right).$$

Our next step must be to find the expression resulting from the terms containing S in the elimination of R.

We shall begin by assuming S to be a spherical harmonic of the form $\mathrm{Q}_n{}^\sigma$, and shall again take the parts depending on γ, γ' separately. Independently of both these quantities, we have

$$\frac{d}{d\theta}\sin\theta\frac{d\mathrm{Q}_n{}^\sigma}{d\theta} + \frac{1}{\sin\theta}\frac{d^2\mathrm{Q}_n{}^\sigma}{d\lambda^2} = -n\,.\,n+1\,.\,\sin\theta\mathrm{Q}_n{}^\sigma \quad . \quad . \quad . \quad . \quad (27).$$

As factor of γ' we have

$$\frac{d}{d\theta}\sin\theta\cos\theta\frac{d\mathrm{Q}_n{}^\sigma}{d\theta} + \cot\theta\frac{d^2\mathrm{Q}_n{}^\sigma}{d\lambda^2}.$$

The value of this has been obtained under (25).

Finally, as factor of γ, we have

$$\frac{d}{d\theta}\sin^2\theta\cos\lambda\frac{d\mathrm{Q}_n{}^\sigma}{d\theta} + \frac{d}{d\lambda}\cos\lambda\frac{d\mathrm{Q}_n{}^\sigma}{d\lambda}.$$

This is identical with the expression (19), the result of the operation being given by (22).

If we collect our results, by adding the right-hand side of (27) to (25) and (22) after applying the appropriate factor, we shall have obtained an expression for

$$\frac{d}{d\theta}\rho\sin\theta\frac{d\mathrm{Q}_n{}^\sigma}{d\theta} + \frac{1}{\sin\theta}\cdot\frac{d}{d\lambda}\cdot\rho\frac{d\mathrm{Q}_n{}^\sigma}{d\lambda} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28).$$

It will appear that S can be expressed in the form of a series

$$\mathrm{S} = \kappa_n{}^0\cos\alpha\mathrm{Q}_n{}^0 + \sum_{\sigma=1}^{\sigma=\infty}\left\{\kappa_n{}^\sigma\cos\left(\sigma\lambda-\alpha\right) + \mu_n{}^\sigma\cos\left(\sigma\lambda+\alpha\right)\right\}\mathrm{Q}_n{}^\sigma \quad . \quad . \quad . \quad (29),$$

where α is determined by the phase of the velocity potential $\psi_n{}^\sigma\sin\left(\sigma\lambda-\sigma\right)$, which rules the flow of matter in which the electric currents are induced. We shall avoid the labour involved in the consideration of special cases if we write (29) in the form

$$\mathrm{S} = \sum_{\sigma=-\infty}^{\sigma=+\infty}\kappa_n{}^\sigma\mathrm{Q}_n{}^\sigma\cos\left(\sigma\lambda-\alpha\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30).$$

Adopting the definition (23) for Q_n^σ, where σ is negative, we may return to the original form by replacing the μ coefficients with the help of

$$\kappa_n^{-\sigma} = (-1)^\sigma \frac{(n+\sigma)!}{(n-\sigma)!} \mu_n^\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31).$$

If each term of (30) be subjected separately to the operation (28) and the results collected, so that all terms depending on any one value Q_n^σ are brought together, we may express the result of the operation by a series of the form

$$-\sum_{\sigma=-\infty}^{\sigma=+\infty} E_n^\sigma Q_n^\sigma \sin\theta \cos(\sigma\lambda - \alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32),$$

which must be equal to (26).

If we put

$$E_n^\sigma = A_n^\sigma + B_n^\sigma \gamma' + C_n^\sigma \gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33),$$

we find

$$A_n^\sigma = n(n+1)\kappa_n^\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34),$$

$$B_n^\sigma = \frac{(n-1)(n+1)(n-\sigma)}{2n-1} \kappa^\sigma{}_{n-1} + \frac{n(n+2)(n+\sigma+1)}{2n+3} \kappa^\sigma{}_{n+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35),$$

$$C_n^\sigma = \frac{(n-1)(n+1)}{2 \,.\, 2n-1} \kappa_{n-1}^{\sigma-1} - \frac{n \,.\, n+2}{2 \,.\, 2n+3} \kappa_{n+1}^{\sigma-1} + \frac{n \,.\, (n+2)(n+\sigma+1)(n+\sigma+2)}{2 \,.\, 2n+3} \kappa_{n+1}^{\sigma+1}$$
$$- \frac{(n-1)(n+1)(n-\sigma)(n-\sigma-1)}{2 \,.\, 2n-1} \kappa_{n-1}^{\sigma+1}. \quad . \quad . \quad (36).$$

The values of κ which determine S may now be found by equating the factors of $\sin\theta Q_n^\sigma$ in (33) to the corresponding factor of $\sin\theta\psi_n^\sigma$ in (26), remembering, however, that in the latter equation σ and n have the definite value belonging to the assumed velocity potential. If, for the sake of clearness, the type and degree of this velocity potential be now denoted by τ and m, we find

$$\left.\begin{array}{ll} E_m^\tau = \tau & 2(2m+1)E_{m-1}^{\tau-1} = -(m+\tau)(m+\tau-1)(m-2\tau+1)\gamma \\ (2m+1)E^\tau{}_{m-1} = 2\tau(m+\tau)\gamma' & 2(2m+1)E_{m+1}^{\tau-1} = -(m+2\tau)(m-\tau+1)(m-\tau+2)\gamma \\ (2m+1)E^\tau{}_{m+1} = 2\tau(m-\tau+1)\gamma' & 2(2m+1)E_{m-1}^{\tau+1} = -(m+2\tau+1)\gamma \\ & 2(2m+1)E_{m+1}^{\tau+1} = -(m-2\tau)\gamma \end{array}\right\} (37).$$

If in any of these values of E the index is less than the suffix, that value may be put equal to zero, as the tesseral function to which that coefficient applies is zero. All other values of E_n^σ are zero. If we take the case $\tau = 1$, $m = 1$, as an example, we obtain from (33), (34), (35), and (36) a number of equations in which all values of E_n^σ may be put equal to zero excepting E_1^1, E_2^1, E_2^0, E_2^2; the values of these are obtained from (37) and we thus find equation (33) for these special values of n and σ to become

$$\begin{aligned}
2\kappa_1{}^1+\tfrac{9}{5}\gamma'\kappa_2{}^1-\gamma\left(\tfrac{3}{10}\kappa_2{}^0-\tfrac{18}{5}\kappa_2{}^2\right) &= 1,\\
6\kappa_2{}^1+\gamma'\left(\kappa_1{}^1+\tfrac{32}{7}\kappa_3{}^1\right)+\gamma\left(\tfrac{1}{2}\kappa_1{}^0-\tfrac{4}{7}\kappa_3{}^0+\tfrac{80}{7}\kappa_3{}^2\right) &= \tfrac{2}{3}\gamma',\\
6\kappa_2{}^0+\gamma'\left(2\kappa_1{}^0+\tfrac{24}{7}\kappa_3{}^0\right)+\gamma\left(\tfrac{48}{7}\kappa_3{}^1-\kappa_1{}^1\right) &= -\gamma,\\
6\kappa_2{}^2+\tfrac{40}{7}\gamma'\kappa_3{}^2+\gamma\left(\tfrac{1}{2}\kappa_1{}^1-\tfrac{4}{7}\kappa_3{}^1+\tfrac{120}{7}\kappa_3{}^3\right) &= \tfrac{1}{6}\gamma.
\end{aligned}$$

These and all similar equations in which the right-hand side is equated to zero are sufficient to determine the κ coefficients, each in terms of a series proceeding by powers of γ and γ'. I proceed to show how the successive approximations may be obtained. If γ and γ' are both zero, the first of the above equations leads to $\kappa_1{}^1=\frac{1}{2}$, and, as the equation must hold for all values of γ, this gives us that portion of $\kappa_1{}^1$ which is independent of γ and γ'. The remaining equations tell us that there can be no other factor κ which has a term not containing γ and γ'. The last three equations contain $\kappa_1{}^1$ and they are the only equations out of the complete series which contain this particular factor. Substituting its value as far as it has been found and neglecting in the brackets all factors except $\kappa_1{}^1$, because they must all depend on γ or γ', and therefore introduce quantities of the second order, we obtain a set of three equations which determines those coefficients which involve the first powers of these quantities. We are thus led to

$$\kappa_2{}^0=-\tfrac{1}{12}\gamma\,;\quad \kappa_2{}^1=\tfrac{1}{36}\gamma'\,;\quad \kappa_2{}^2=\tfrac{1}{72}\gamma.$$

No other coefficients can contain terms depending on first powers. If we now write down all equations in which $\kappa_2{}^0$, $\kappa_2{}^1$, $\kappa_2{}^2$ occur, we may determine the terms involving γ^2, $\gamma\gamma'$ and γ'^2. Thus if the above equation involving $\kappa_1{}^1$ is reconsidered, we find that in view of our knowledge just acquired $\kappa_1{}^1$ must contain terms in γ^2 and γ'^2 satisfying the equation

$$2\kappa_1{}^1+\tfrac{1}{20}\gamma'^2-\tfrac{1}{40}\gamma^2=0.$$

The equations for E'_3, $E_3{}^3$, $E_3{}^{-1}$, give

$$\begin{aligned}
12\kappa_3{}^1+\gamma'\left(\tfrac{16}{5}\kappa_2{}^1+\tfrac{25}{3}\kappa_4{}^1\right)+\gamma\left(\tfrac{4}{5}\kappa_2{}^0-\tfrac{5}{6}\kappa_4{}^0+25\kappa_4{}^2-\tfrac{8}{5}\kappa_2{}^2\right) &= 0,\\
12\kappa_3{}^2+\gamma'\left(\tfrac{8}{5}\kappa_2{}^2+10\kappa_4{}^2\right)+\gamma\left(\tfrac{4}{5}\kappa_2{}^1-\tfrac{5}{6}\kappa_4{}^1+35\kappa_4{}^3\right) &= 0,\\
12\kappa_3{}^3+\tfrac{35}{3}\gamma'\kappa_4{}^3+\gamma\left(\tfrac{4}{5}\kappa_2{}^2-\tfrac{5}{6}\kappa_4{}^2+\tfrac{140}{3}\kappa_4{}^4\right) &= 0,\\
12\kappa_3{}^{-1}+\gamma'\left(\tfrac{32}{5}\kappa_2{}^{-1}+5\kappa_4{}^{-1}\right)+\gamma\left(\tfrac{4}{5}\kappa_2{}^{-2}-\tfrac{5}{6}\kappa_4{}^{-2}+10\kappa_4{}^0-\tfrac{48}{5}\kappa_2{}^0\right) &= 0.
\end{aligned}$$

The factors such as $\kappa_4{}^0$, $\kappa_2{}^{-2}$, $\kappa_4{}^{-2}$, which can only contain powers of γ and γ' higher than the first may be left out of account in solving these equations, and we thus find all terms which contain γ^2, γ'^2 or $\gamma\gamma'$. We may proceed in this manner, gradually working by successive approximations from lower to higher powers. The following two tables contain the results, including all powers as far as the third, for the two typical atmospheric motions represented by the current functions $\psi_1{}^1$ and $\psi_2{}^2$. For convenience of use the μ coefficients now replace the κ coefficients with negative indices.

Values of κ_n^σ. (Velocity Potential = ψ_1^1.)

$n =$	1	2	3	4
$\sigma = 0$	$\frac{1}{40}\gamma\gamma'$	$-\frac{1}{12}\gamma - \frac{89}{3024}\gamma\gamma'^2 - \frac{2}{189}\gamma^3$	$\frac{2}{45}\gamma\gamma'$	$\frac{1}{168}\gamma^3 - \frac{1}{42}\gamma\gamma'^2$
1	$\frac{1}{2} + \frac{1}{80}\gamma^2 - \frac{1}{40}\gamma'^2$	$\frac{1}{36}\gamma' + \frac{89}{48 \times 189}\gamma'^3 - \frac{25}{48 \times 189}\gamma'\gamma^2$	$\frac{1}{270}\gamma^2 - \frac{1}{135}\gamma'^2$	$-\frac{1}{280}\gamma'\gamma^2 + \frac{1}{420}\gamma'^3$
2	—	$-\frac{1}{72}\gamma - \frac{121}{189 \times 192}\gamma^3 - \frac{25}{96 \times 189}\gamma\gamma'^2$	0	$-\frac{1}{14 \times 720}\gamma^3 + \frac{1}{14 \times 180}\gamma\gamma'^2$
3	—	—	$\frac{1}{1080}\gamma^2$	$-\frac{1}{14 \times 720}\gamma'\gamma^2$
4	—	—	—	$-\frac{1}{72 \times 280}\gamma^3$

Values of μ_n^σ. (Velocity Potential = ψ_1^1.)

$n =$	1	2	3	4
$\sigma = 1$	$-\frac{\gamma^2}{80}$	0	$\frac{\gamma^2}{180}$	$-\frac{1}{240}\gamma'\gamma^2$
$\sigma = 2$	—	$\frac{19}{64 \times 189}\gamma^3$	0	$\frac{1}{14 \times 240}\gamma^3$

Values of κ_n^σ. (Velocity Potential = ψ_2^2.)

$n =$	1	2	3	4	5
$\sigma = 0$	$-\frac{4}{105}\gamma^2\gamma'$	$\frac{4}{63}\gamma^2$	$-\frac{29}{720}\gamma^2\gamma'$	$-\frac{1}{28}\gamma^2$	$\frac{4}{105}\gamma'\gamma^2$
1	$-\frac{1}{105}\gamma^3$	0	$-\frac{1}{18}\gamma - \frac{133}{36 \times 360}\gamma^3 - \frac{133}{36 \times 360}\gamma\gamma'^2$	$\frac{1}{40}\gamma\gamma'$	$\frac{1}{350}\gamma^3 - \frac{2}{175}\gamma\gamma'^2$
2	—	$\frac{1}{3} + \frac{2}{189}\gamma^2 - \frac{4}{189}\gamma'^2$	$\frac{1}{45}\gamma' + \frac{11}{1620}\gamma'^3 + \frac{1}{48 \times 270}\gamma'\gamma^2$	$\frac{1}{420}\gamma^2 - \frac{1}{210}\gamma'^2$	$-\frac{1}{525}\gamma'\gamma^2 + \frac{2}{1575}\gamma'^3$
3	—	—	$-\frac{1}{180}\gamma - \frac{11}{36 \times 180}\gamma^3 + \frac{43}{16 \times 36 \times 45}\gamma\gamma'^2$	$-\frac{1}{1680}\gamma\gamma'$	$-\frac{1}{12600}\gamma^3 + \frac{1}{315}\gamma\gamma'^2$
4	—	—	—	$\frac{1}{3360}\gamma^2$	0
5	—	—	—	—	$-\frac{1}{45 \times 1680}\gamma^3$

VALUES of μ_n^σ. (Velocity Potential = ψ_2^2.)

$n =$	1	3	5
$\sigma = 1$	$\frac{1}{105}\gamma^3$	$-\frac{29}{12 \times 360}\gamma^3$	$\frac{1}{630}\gamma^3$

The determination of S is only of interest as a stepping stone to the evaluation of R. We must therefore return to the first of equations (14), and by its means determine $dR/d\lambda$ as a series of harmonics in the normal form.

If we write the velocity potential $\psi_m^\tau \sin(\tau\lambda-\alpha)$, we find by means of the formulæ of transformation previously introduced

$$\begin{aligned}
\rho \cos\theta \frac{d\psi}{d\lambda} = {} & \frac{(m-\tau+1)\,\psi^\tau_{m+1}+(m+\tau)\,\psi^\tau_{m-1}}{2m+1}\,\tau\cos(\tau\lambda-\alpha) \\
& + \left\{(m-\tau+1)\frac{(m-\tau+2)\,\psi^\tau_{m+2}+(m+\tau+1)\,\psi_m^\tau}{(2m+1)(2m+3)}\right. \\
& \qquad \left. +(m+\tau)\frac{(m-\tau)\,\psi_m^\tau+(m+\tau-1)\,\psi^\tau_{m-2}}{(2m-1)(2m+1)}\right\}\gamma'\tau\cos(\tau\lambda-\alpha) \\
& + \left\{(m-\tau+1)\frac{(\psi_{m+2}^{\tau+1}-\psi_m^{\tau+1})}{2\,(2m+1)(2m+3)}\right. \\
& \qquad \left. +(m+\tau)\frac{(\psi_m^{\tau+1}-\psi_{m-2}^{\tau+1})}{2\,.\,(2m-1)(2m+1)}\right\}\gamma\tau\cos\{(\tau+1)\lambda-\alpha\} \\
& + \left\{(m-\tau+1)\frac{(m+\tau)(m+\tau+1)\,\psi_m^{\tau-1}-(m-\tau+2)(m-\tau+3)\,\psi_{m+2}^{\tau-1}}{2\,(2m+1)(2m+3)}\right. \\
& \qquad \left. +(m+\tau)\frac{(m+\tau-1)(m+\tau-2)\,\psi_{m-2}^{\tau-1}-(m-\tau)(m-\tau+1)\,\psi_m^{\tau-1}}{2\,.\,(2m-1)(2m+1)}\right\} \\
& \qquad \gamma\tau\cos\{(\tau-1)\lambda-\alpha\} \quad . \quad . \quad (37\ bis).
\end{aligned}$$

As, omitting constant factors, ψ_n^σ is equal to Q_n^σ, the tesseral function of type σ and degree n, we may now write

$$\rho\cos\theta\frac{d\psi}{d\lambda} = \Sigma f_n^\sigma Q_n^\sigma,$$

and tabulate those values of f_n^σ which are not equal to zero. The following table is constructed in this way.

Values of $f_n{}^\sigma$.

$n\,;\ \sigma =$	$\tau - 1$	τ	$\tau + 1$
$m-2$	$\frac{(m+\tau)(m+\tau-1)(m+\tau-2}{2(2m-1)(2m+1)}\tau\gamma$	$\frac{(m+\tau)(m+\tau-1)}{(2m-1)(2m+1)}\tau\gamma'$	$-\frac{m+\tau}{2(2m-1)(2m+1)}\tau\gamma$
$m-1$	—	$\frac{m+\tau}{2m+1}\tau$	—
m	$\frac{(m+\tau)(m-\tau+1)}{2(2m-1)(2m+3)}\tau(2\tau-1)\gamma$	$\frac{2(m^2-\tau^2)+(2m-1)}{(2m-1)(2m+3)}\tau\gamma$	$\frac{2\tau-1}{2(2m-1)(2m+3)}\tau\gamma$
$m+1$	—	$\frac{(m-\tau+1)}{2m+1}\tau$	—
$m+2$	$-\frac{(m-\tau+2)(m-\tau+3)}{2(2m+1)(2m+3)}\tau\gamma$	$\frac{(m-\tau+1)(m-\tau+2)}{(2m+1)(2m+3)}$	$\frac{(m-\tau+1)}{2(2m+1)(2m+2)}\tau\gamma$

The transformation of $-\rho\sin\theta\dfrac{d\mathrm{S}}{d\theta}$ presents no difficulties. If S be expressed in its series according to (30) and the terms re-arranged, the result of the operation is of the form $\Sigma r_n{}^\sigma \mathrm{Q}_n{}^\sigma$, where $r_n{}^\sigma$ is made up of three parts. Independently of γ and γ', we have

$$\frac{(n+2)(n+\sigma+1)}{2n+3}\kappa^\sigma{}_{n+1} - \frac{(n-1)(n-\sigma)}{2n-1}\kappa^\sigma{}_{n-1} \quad . \quad . \quad . \quad . \quad . \quad (38).$$

We have further, multiplied by γ',

$$\frac{n+\sigma+1}{2n+3}\left[\frac{(n+3)(n+\sigma+2)}{2n+5}\kappa^\sigma{}_{n+2} - \frac{n(n-\sigma+1)}{2n+1}\kappa_n{}^\sigma\right]$$
$$+\frac{n-\sigma}{2n-1}\left[\frac{(n+1)(n+\sigma)}{2n+1}\kappa_n{}^\sigma - \frac{(n-2)(n-\sigma-1)}{2n-3}\kappa^\sigma{}_{n-2}\right] \quad . \quad . \quad (39),$$

and finally, multiplied by γ,

$$\frac{(n+\sigma+1)(n+\sigma+2)}{2\,.\,2n+3}\left[\frac{(n+3)(n+\sigma+3)}{2n+5}\kappa_{n+2}{}^{\sigma+1} - \frac{n(n-\sigma)}{2n+1}\kappa_n{}^{\sigma+1}\right]$$
$$-\frac{(n-\sigma)(n-\sigma-1)}{2(2n-1)}\left[\frac{(n+1)(n+\sigma+1)}{2n+1}\kappa_n{}^{\sigma+1} - \frac{(n-2)(n-\sigma-2)}{2n-3}\kappa_{n-2}{}^{\sigma+1}\right]$$
$$-\frac{1}{2\,.\,2n+3}\left[\frac{(n+3)(n+\sigma+1)}{2n+5}\kappa_{n+2}{}^{\sigma-1} - \frac{n(n-\sigma+2)}{2n+1}\kappa_n{}^{\sigma-1}\right]$$
$$+\frac{1}{2(2n-1)}\left[\frac{(n+1)(n+\sigma-1)}{2n+1}\kappa_n{}^{\sigma-1} - \frac{(n-2)(n-\sigma)}{2n-3}\kappa_{n-2}{}^{\sigma-1}\right] \quad . \quad . \quad . \quad . \quad (40).$$

By means of the values of κ already tabulated, the factors r may be calculated.

R is expressible in the form

$$\mathrm{R} = \sum_{\sigma=0}^{\sigma=\infty} \{p_n^\sigma \sin(\sigma\lambda-\alpha)+q_n^\sigma \sin(\sigma\lambda+\alpha)\}\, \mathrm{Q}_n^\sigma \ldots,$$

or, admitting negative values of σ, more conveniently by

$$\mathrm{R} = \sum_{\sigma=-\infty}^{\sigma=+\infty} p_n^\sigma \mathrm{Q}_n^\sigma \sin(\sigma\lambda-\alpha).$$

In the ultimate result we return to the q coefficients through the relation

$$p_n^{-\sigma} = (-1)^{\sigma+1} \frac{(n+\sigma)\,!}{(n-\sigma)\,!} q_n^\sigma.$$

Equating the factors of $\mathrm{Q}_n^\sigma \cos\sigma(\lambda-\alpha)$ in (14), we now find

$$\sigma p_n^\sigma = f_n^\sigma + r_n^\sigma.$$

The calculation of r_n^σ in its present form involves the summation of the expressions (38), (39), and (40), the κ factors being substituted out of the tables previously given. The somewhat troublesome labour involved in this process may almost entirely be avoided by a transformation of expression (38). Substituting A_n^σ from (34) into (33), we find

$$n\,.\,n+1\,.\,\kappa_n^\sigma = \mathrm{E}_n^\sigma - \mathrm{B}_n^\sigma\gamma' - \mathrm{C}_n^\sigma\gamma,$$

and by means of this equation, when $n+1$ and $n-1$ are respectively substituted for m, we obtain

$$\frac{(n+2)(n+\sigma+1)}{2n+3}\kappa^\sigma_{\ n+1} - \frac{(n-1)(n-\sigma)}{2n-1}\kappa^\sigma_{\ n-1} = e_n^\sigma + (\mathrm{B}^\sigma_{\ n-1} - \mathrm{B}^\sigma_{\ n+1})\gamma' + (\mathrm{C}^\sigma_{\ n-1} + \mathrm{C}^\sigma_{\ n+1})\gamma \quad (41),$$

where

$$e_n^\sigma = \frac{n+\sigma+1}{(n+1)(2n+3)}\mathrm{E}^\sigma_{\ n+1} - \frac{(n-\sigma)}{n(2n-1)}\mathrm{E}^\sigma_{\ n-1}.$$

If the right-hand side of (41) replaces (38), and is added to (39) and (40), the whole expression reduces to

$$r_n^\sigma = e_n^\sigma + \frac{1}{n\,.\,n+1}\left[\tfrac{1}{2}\sigma\gamma\,\{\kappa_n^{\sigma-1} + (n-\sigma)(n+\sigma+1)\,\kappa_n^{\ +1}\} - \sigma^2\gamma'\kappa_n^\sigma\right].$$

We have, therefore, the following very convenient expression which allows us to calculate the p coefficients from the previously established values of κ :—

$$p_n^\sigma = \frac{1}{\sigma}(e_n^\sigma + f_n^\sigma) + \frac{1}{n\,.\,n+1}\left[\tfrac{1}{2}\gamma\,\{\kappa_n^{\sigma-1} + (n-\sigma)(n+\sigma+1)\,\kappa_n^{\sigma+1}\} - \sigma\gamma'\kappa_n^\sigma\right] \quad (42).$$

The first term on the right-hand side is zero, except for the cases where the type σ

does not differ by more than 1 and the degree n by not more than 2 from the type and degree of the original velocity potential.

For the calculation of these special cases the previous investigation furnishes the necessary formulæ. Confining ourselves to the velocity potentials ψ_1^1 and ψ_2^2, we find the requisite numbers collected in the following table :—

VALUES of $e_n^\sigma + f_n^\sigma$.

Velocity potential $= \psi_1^1$.			Velocity potential $= \psi_2^2$.			
$\sigma =$	1	2	$\sigma =$	1	2	3
$n = 1$	$\frac{2}{5}\gamma'$	—	$n = 2$	$\frac{1}{7}\gamma$	$\frac{10}{21}\gamma'$	—
2	$\frac{1}{6}$	—	3	—	$\frac{4}{15}$	—
3	$\frac{2}{45}\gamma'$	$\frac{1}{45}\gamma$	4	$-\frac{3}{70}\gamma$	$\frac{2}{35}\gamma'$	$\frac{3}{140}\gamma'$

Equation (42) holds also for negative values of σ, but when σ is smaller than -2, it is more convenient to calculate the q coefficients from the values of μ_n^σ already given. We find for this case

$$q_n^\sigma = \frac{1}{n \,.\, n+1} \left[\tfrac{1}{2}\gamma \left\{\mu_n^{\sigma-1} + (n+\sigma+1)(n-\sigma)\,\mu_n^{\sigma+1}\right\} - \sigma\gamma'\mu_n^\sigma\right],$$

which, as may be expected, is identical with the equation connecting p and κ.

For $\sigma = 1$, (42) gives

$$p_n^{-1} = \frac{1}{n \,.\, n+1} \left[\tfrac{1}{2}\gamma \left\{\kappa_n^{-2} + n\,(n+1)\,\kappa_n^0\right\} + \gamma'\kappa_n^{-1}\right]$$

$$= \tfrac{1}{2}\gamma \left\{(n-1)(n+2)\,\mu_n^2 + \kappa_n^0\right\} - \gamma'\mu'_n,$$

and hence

$$q'_n = \frac{1}{n \,.\, n+1} \left[\tfrac{1}{2}\gamma \left\{(n-1)(n+2)\,\mu_n^2 + \kappa_n^0\right\} - \gamma'\mu'_n\right]. \quad . \quad . \quad . \quad . \quad (43).$$

Our equations are not valid for the case $\sigma = 0$, because they depend on a division by σ. The first of equations (14) from which we started containing R only in the form $d\mathrm{R}/d\lambda$ is obviously unsuitable to determine those parts of R which are independent of λ; we must, therefore, have recourse to the second equation

$$\frac{d\mathrm{R}}{d\theta} = \rho \cos\theta \frac{d\psi}{d\theta} + \rho \frac{d\mathrm{S}}{\sin\theta \, d\lambda}.$$

Such products as $\rho \frac{d\psi}{d\lambda}$ and $\rho \frac{d\mathrm{S}}{d\lambda}$ may give rise to terms independent of λ only through products of the form $\cos\lambda \cos(\lambda-\alpha)$, $\cos\lambda\cos(\lambda+\alpha)$ or $\cos\lambda\sin(\lambda-\alpha)$, $\cos\lambda\sin(\lambda+\alpha)$.

We need therefore only consider that part of ρ which involves $\cos\lambda$ and terms of the first type in ψ and S. Selecting the two terms $\{\kappa'_n \cos(\lambda-\alpha)+\mu'_2\cos(\lambda+\alpha)\}\,\mathrm{Q}'_n$ in the expression for S and rejecting all terms not containing λ, we are left with

$$\frac{\rho\, d\mathrm{S}}{\sin\theta\, d\lambda} = \tfrac{1}{2}\gamma\,(\mu'_n-\kappa'_n)\,\mathrm{Q}'_n \sin\alpha.$$

Similarly

$$\rho\cos\theta\frac{d\psi}{d\theta} = -\tfrac{1}{2}\sin\theta\cos\theta\frac{d\mathrm{Q}'_m}{d\theta}\sin\alpha.$$

By means of the formulæ of transformation previously given we find

$$-\sin\theta\cos\theta\frac{d\mathrm{Q}'_m}{d\theta} = \frac{m\,.\,(m+1)^2}{(2m+1)(2m-1)}\mathrm{Q}'_{m-2}+\frac{m^2+m-3}{(2m-1)(2m+3)}\mathrm{Q}'_m-\frac{m^2(m+1)}{(2m+1)(2m+3)}\mathrm{Q}'_{m+2}.$$

In the special case worked out in the previous pages in which $m = 1$,

$$-\tfrac{1}{2}\sin\theta\cos\theta\frac{d\mathrm{Q}'_1}{d\theta} = -\tfrac{1}{10}\mathrm{Q}'_1-\tfrac{1}{15}\mathrm{Q}'_3.$$

The velocity potential ψ_2^2 contributes, as far as the term $\rho\cos\theta\frac{d\psi}{d\theta}$ is concerned, nothing to the zonal harmonics in R.

We have therefore in the second case, and whenever the velocity potential does not contain a term of the first type,

$$\frac{d\mathrm{R}}{d\theta} = \tfrac{1}{2}\gamma\,(\kappa'_n-\mu'_n)\,\mathrm{Q}'_n\sin\alpha.$$

If R, as far as its zonal harmonics are concerned, is written in the form $\Sigma p_n^0 \mathrm{P}_n \sin\alpha$, we find, as $-\frac{d\mathrm{P}_n}{d\theta} = \sin\theta\frac{d\mathrm{P}_n}{d\mu} = \mathrm{Q}'_n$,

$$p_n^0 = \tfrac{1}{2}\gamma\,(\kappa'_n-\mu'_n) \quad \ldots\ldots\ldots\ldots \quad (44).$$

We should have obtained the same value if we had applied the general equation to this case. When $\tau = 1$, we have to consider the terms depending on $\frac{d\psi}{d\theta}$, and must therefore write

$$p_1^0 = \{-\tfrac{1}{10}+\tfrac{1}{2}(\kappa'_1-\mu'_1)\}\,\gamma,$$

$$p_3^0 = \{-\tfrac{1}{15}+\tfrac{1}{2}(\kappa'_3-\mu'_3)\}\,\gamma.$$

For all other values of n equation (44) applies.

The tables which follow give the calculated values of p_n^σ and q_n^σ, and therefore solve the problem as far as terms of the fourth order in γ and γ'. It will be noticed that for unity, which is the highest admissible value of γ and γ', all the factors involving higher powers than the first are so small that their effect falls much below anything that observation is capable of showing. Hence the approximate calculation given in Part I. is sufficient for all practical purposes.

Restoring constant factors, we may summarise the result of the previous investigation as follows :—

1. *Notation.*

Q_n^σ denotes the tesseral function $\sin^\sigma \theta \, d^\sigma P_n/d\mu^\sigma$, where P_n is the zonal harmonic of degree n, and θ the colatitude.

C measured upwards denotes the vertical magnetic force of the earth's permanent field at the geographical pole.

e is the thickness of the conducting atmospheric shell.

ρ is the conductivity, which is supposed to be variable and depending on θ and the local time $\lambda+t$, according to the relation $\rho = \rho_0 [1+\gamma' \cos \theta+\gamma \sin \theta \cos (\lambda+t)]$, where γ and γ' are constant.

$A_n^\sigma Q_n^\sigma \cos \{\sigma(\lambda+t)-\alpha\}$ is the velocity potential of the flow of air.

2. *Conclusion.*

The current function R of electric flow induced under the action of the vertical force C cos θ in the oscillating shell of air is then expressed as a sum

$$R = A_n^\sigma C e \rho_0 \left[\sum_{\sigma=0}^{\sigma=\infty} p_n^\sigma Q_n^\sigma \sin \{\sigma(\lambda+t)-\alpha\} + \sum_{\sigma=1}^{\sigma=\infty} q_n^\sigma Q_n^\sigma \sin \{\sigma(\lambda+t)+\alpha\}\right].$$

In order to obtain the magnetic potential of the variation caused by the flow of air, a factor $-4\pi(n+1)/(2n+1)$ has to be applied.

The factors p_n^σ and q_n^σ are given in the tables (including terms of the fourth order of γ and γ') for the velocity potentials

$$A'_1 Q' = A'_1 \sin \theta \cos \{(\lambda+t)-\alpha\}$$

and

$$A_2^2 Q_2^2 = 3A_2^2 \sin^2 \theta \cos \{2(\lambda+t)-\alpha\}.$$

I. VELOCITY Potential: $A_1 \sin\theta \cos\{(\lambda+t)-\alpha\}$.

$$p_1^0 = \frac{3}{20}\gamma + \frac{1}{80}\gamma^3 - \frac{1}{80}\gamma\gamma'^2.$$

$$p_2^0 = \frac{1}{72}\gamma\gamma' + \frac{89}{18144}\gamma\gamma'^3 - \frac{25}{18144}\gamma'\gamma^3.$$

$$p_3^0 = -\frac{1}{15}\gamma - \frac{1}{1080}\gamma^3 - \frac{1}{270}\gamma'^2\gamma.$$

$$p_4^0 = \frac{1}{3360}\gamma'\gamma^3 + \frac{1}{840}\gamma'^3\gamma.$$

$$p_1^1 = \frac{3}{20}\gamma' + \frac{1}{80}\gamma'^3.$$

$$p_2^1 = \frac{1}{6} - \frac{1}{216}\gamma'^2 - \frac{5}{432}\gamma^2 - \frac{89}{54432}\gamma'^4 - \frac{31}{15552}\gamma^4 - \frac{89}{36288}\gamma^2\gamma'^2.$$

$$p_3^1 = \frac{2}{45}\gamma' + \frac{1}{648}\gamma'\gamma^2 + \frac{1}{1620}\gamma'^3.$$

$$p_4^1 = -\frac{1}{4200}\gamma^2\gamma'^2 - \frac{1}{8400}\gamma'^4 + \frac{1}{9600}\gamma^4.$$

$$p_2^2 = \frac{1}{144}\gamma\gamma' + \frac{1}{1134}\gamma'\gamma^3 + \frac{139}{108864}\gamma\gamma'^3.$$

$$p_3^2 = \frac{1}{90}\gamma + \frac{1}{2592}\gamma^3 - \frac{1}{3240}\gamma\gamma'^2.$$

$$p_4^2 = -\frac{23}{201600}\gamma'\gamma^3 + \frac{1}{50400}\gamma\gamma'^3.$$

$$p_3^3 = -\frac{1}{4320}\gamma'\gamma^2.$$

$$p_4^3 = \frac{1}{40320}\gamma^2\gamma'^2 - \frac{1}{80640}\gamma^4.$$

$$p_4^4 = \frac{1}{134400}\gamma'\gamma^3.$$

$$q_1^1 = \frac{1}{80}\gamma^2\gamma'.$$

$$q_2^1 = -\frac{1}{144}\gamma^2 - \frac{89}{36288}\gamma^2\gamma'^2 - \frac{13}{36288}\gamma^4.$$

$$q_3^1 = \frac{1}{720}\gamma^2\gamma'.$$

$$q_4^1 = -\frac{13}{33600}\gamma^2\gamma'^2 + \frac{19}{67200}\gamma^4.$$

$$q_2^2 = -\frac{19}{36288}\gamma'\gamma^3.$$

$$q_3^2 = \frac{1}{4320}\gamma^3.$$

$$q_4^2 = -\frac{9}{67200}\gamma'\gamma^3.$$

$$q_3^3 = 0.$$

$$q_4^3 = \frac{1}{134400}\gamma^4.$$

II. Velocity Potential: $3A_2^2 \sin^2 \theta \cos\{2(\lambda+t)-\alpha\}$.

$$p_1^0 = -\frac{1}{105}\gamma^4.$$

$$p_2^0 = 0.$$

$$p_3^0 = -\frac{1}{36}\gamma^2 - \frac{23}{12960}\gamma^4 - \frac{133}{25920}\gamma^2\gamma'^2.$$

$$p_4^0 = \frac{1}{80}\gamma'\gamma^2.$$

$$p_5^0 = -\frac{1}{175}\gamma^2\gamma'^2 + \frac{1}{1575}\gamma^4.$$

$$p_1^1 = -\frac{1}{210}\gamma'\gamma^3.$$

$$p_2^1 = \frac{16}{63}\gamma - \frac{4}{567}\gamma\gamma'^2 + \frac{5}{567}\gamma^3.$$

$$p_3^1 = \frac{1}{72}\gamma\gamma' - \frac{41}{51840}\gamma'\gamma^3 + \frac{191}{51840}\gamma\gamma'^3.$$

$$p_4^1 = -\frac{3}{70}\gamma + \frac{1}{5600}\gamma^3 - \frac{19}{5600}\gamma\gamma'^2.$$

$$p_5^1 = \frac{23}{23625}\gamma\gamma'^3 - \frac{11}{31500}\gamma'\gamma^3.$$

$$p_2^2 = \frac{8}{63}\gamma' - \frac{2}{567}\gamma^2\gamma' + \frac{4}{567}\gamma'^3.$$

$$p_3^2 = \frac{2}{15} - \frac{1}{270}\gamma'^2 - \frac{1}{270}\gamma^2 - \frac{1}{38880}\gamma'^2\gamma^2 - \frac{53}{62208}\gamma^4 - \frac{11}{9720}\gamma'^4.$$

$$p_4^2 = \frac{1}{35}\gamma' + \frac{1}{5600}\gamma'\gamma^2 + \frac{1}{2100}\gamma'^3.$$

$$p_5^2 = \frac{1}{15750}\gamma^2\gamma'^2 + \frac{1}{63000}\gamma^4 - \frac{2}{23625}\gamma'^4.$$

$$p_3^3 = \frac{1}{432}\gamma\gamma' - \frac{41}{311040}\gamma\gamma'^3 + \frac{133}{311040}\gamma'\gamma^3.$$

$$p_4^3 = \frac{1}{140}\gamma - \frac{1}{33600}\gamma\gamma'^2 + \frac{1}{8400}\gamma^3.$$

$$p_5^3 = -\frac{1}{94500}\gamma\gamma'^3 - \frac{1}{42000}\gamma^3\gamma'.$$

$$p_4^4 = -\frac{1}{13440}\gamma'\gamma^2.$$

$$p_5^4 = +\frac{1}{189000}\gamma^2\gamma'^2 - \frac{1}{283500}\gamma^4.$$

$$p_5^5 = \frac{1}{453600}\gamma'\gamma^3.$$

$$q_1^1 = -\frac{1}{70}\gamma^3\gamma'.$$

$$q_2^1 = \frac{1}{189}\gamma^3.$$

II. VELOCITY Potential: $3A_2^2 \sin^2\theta \cos\{2(\lambda+t)-\alpha\}$ (continued).

$$q_3^1 = -\frac{29}{25920}\gamma^3\gamma'.$$

$$q_4^1 = -\frac{1}{1120}\gamma^3.$$

$$q_5^1 = \frac{11}{18900}\gamma'\gamma^3.$$

$$q_2^2 = 0.$$

$$q_3^2 = -\frac{29}{103680}\gamma^4.$$

$$q_4^2 = 0.$$

$$q_5^2 = \frac{1}{37800}\gamma^4.$$

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By C. Chree, *Sc.D., LL.D., F.R.S., Superintendent Observatory Department, National Physical Laboratory.*

(*From the National Physical Laboratory.*)

Received November 2,—Read December 12, 1907.

Contents.

§ 1. In 1903 I carried out an analysis*—referred to here for brevity as A—of the results given by the Kew magnetographs on "quiet" days during the 11 years 1890 to 1900. This investigation brought to light various novel phenomena. It was subsequently shown—in a paper † to be referred to as B—that these phenomena are equally true of "quiet" days at Falmouth. Some of the phenomena suggested the

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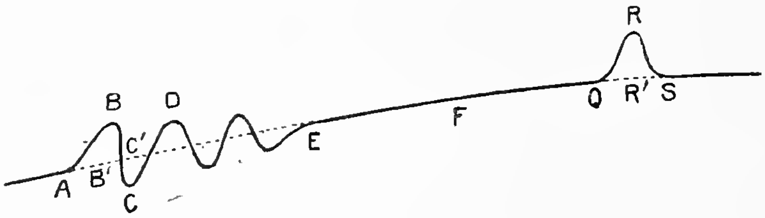
[*] 'Phil. Trans. Roy. Soc.,' A, vol. 202, p. 335, 1903.

[†] 'Phil. Trans. Roy. Soc.,' A, vol. 204, p. 373, 1905.

possibility of differences of a certain kind between quiet days and other undisturbed days, and between ordinary days and disturbed days. To prosecute this enquiry, it was necessary to make an analysis of the data from all days at Kew from 1890 to 1900. Declination being the element of most practical interest, and least open to instrumental uncertainties, it was decided to treat it thoroughly in the first instance.

§ 2. In measuring the quiet day curves at Kew—a practice instituted in 1890—it has been usual to smooth them when any little irregularities occur, by drawing a free-hand pencil trace following the general trend. It was decided, with some hesitation, to continue the practice, so that the results from all days should be as strictly comparable as possible with those from quiet days. The nature of the difficulties will be understood from the accompanying diagram. The continuous line curve ABCDEFQRS represents a hypothetical photographic record. The dotted line AB′C′R′ represents the smoothed curve. When the object aimed at is the regular diurnal inequality, it will probably be generally conceded that the method of smoothing adopted is satisfactory so far as the wave-like portion ABCDE is concerned, at least so long as the interval of time corresponding to this portion is under an hour. If, however, the times from A to B and from B to C were each an hour, the procedure would be disapproved by some authorities, who would argue that the free-hand curve should always be drawn so that its ordinate at any particular hour should represent the arithmetic mean of an infinite number of ordinates, uniformly distributed in time throughout the preceding and succeeding 30 minutes. It should, however, be remembered that the exact instant when an hour falls is really arbitrary. One observer may use Greenwich time, another local, and if the smoothing were carried out in accordance with the view last mentioned, it might make all the difference which choice happened to have been made. A disturbance such as QRS presents difficulties of another kind. If the time interval from Q to S is only a few minutes, and the general trend of the curve is very clearly shown, and closely similar to that of the average day, there can, I think, be little doubt that the best plan—at least when diurnal inequalities are concerned—is simply to disregard the disturbance altogether. If, however, the time from Q to S is considerable, and the general trend of the curve not clearly shown, the appropriate treatment is difficult to determine.



§ 3. The smoothing process was done partly by Mr. Baker, the Chief Assistant, and partly by myself. In some cases even considerable disturbances presented little difficulty, the oscillations being on the whole regular and the general trend of the curve clearly shown; but it was soon apparent that in other cases smoothing would be altogether too arbitrary a process. It was decided to omit such *disturbed* days entirely when calculating the regular diurnal inequality. The days thus omitted numbered 209, or an average of 19 a year.

§ 4. It should be clearly understood that in classifying a day as "disturbed," regard was paid exclusively to the nature and not to the mere magnitude of the disturbance. If the irregular movements were mainly of the type seen at QRS in the diagram on p. 206, or if the declination showed an abnormally high or low value for several successive hours, the curve was classified as disturbed, though the range might be less than in a neighbouring "ordinary" curve where the disturbances approached the type illustrated by ABE of the diagram. That the method of choice is open to criticism, I freely acknowledge. It introduces a personal element, and something unquestionably depends on the individual's freshness and nerve at the moment. If in his best form, he may at once make up his mind how to smooth a disturbed curve, even when heroic rectifications are necessary, whilst if he is tired and hesitates he probably in the end relegates the curve to the disturbed class. The selection of the disturbed days was in every case made by myself, and the curves for a single year were always considered together. Thus I regard the number of disturbed days as more appropriate for determining the relative amount of disturbance at different seasons of the year than for comparing one year with another. I have discussed this question at some length because other criterions for disturbance have been applied. Thus Mr. ELLIS has classified days as disturbed, and as of greater or less disturbance, mainly according to the amplitude of the range, and his classification has been followed by Mr. MAUNDER in his interesting researches into the relationship between sunspots and magnetic storms at Greenwich. At first sight, a reference to amplitude seems a simpler and more satisfactory method than the one that I have adopted, but it is in reality, as I have explained elsewhere, highly arbitrary. This will, I think, be recognised on referring to Table XIV., showing the mean of the *absolute daily ranges* (maximum less minimum) for each month from 1890 to 1900. The mean, it will be seen, varied in individual months from 4′·73 in December, 1900, to 24′·02 in March, 1892, and taking the mean of the twelve months it varied from 9′·17 in 1900 to 17′·70 in 1892. Even restricting ourselves to the Astronomer Royal's quiet days, the mean ranges for August, 1892, and December, 1899, were respectively 15′·20 and 3′·12. A range of 15′ at mid-winter at sunspot minimum *may* imply much more real disturbance than a range of 30′ at the equinox near sunspot maximum.

§ 5. Mr. MAUNDER's list for the years 1890 to 1900 included 150 disturbances. His figures, however, denote not the number of disturbed days, but what he believed to be the number of separate magnetic storms. Disturbed conditions usually last for a good many hours, and not infrequently for two or more days. Thus the number of disturbed days naturally exceeds the number of separate storms. When disturbed conditions last for several days it is sometimes doubtful whether one is dealing with one or with several storms separated by comparatively quiet interludes. If we classify as one storm all groups of successive disturbed days we have 125 storms, two of them extending from one month to the next. The distribution of these and Mr. MAUNDER's storms in the different years is shown in Table I. The difference between the totals for Kew and Greenwich arises of course simply from the method of selection. A considerable number of days treated as "ordinary" at Kew would fairly rank as days of disturbance when regarded from the standpoint either of the amplitude or the number of the oscillatory movements, and would most naturally be classified as disturbed for purposes such as those of Mr. MAUNDER. The chief difference in the totals is for 1892 and 1893, especially the latter year. In 1893, sunspots were at their maximum, and the regular diurnal range was very large. A comparatively trifling disturbance might suffice to bring the range over 20′, which Mr. ELLIS treats, at least roughly, as a minimum value for a disturbance; thus, when main importance was assigned to the amplitude of the range, it was only natural to reach a larger number for the disturbed days in 1893 than when attention was directed to the greater or less abnormality of the curve. As compared to the two adjacent years, 1893 was, in fact, remarkable for the extraordinary absence of irregular movements.

TABLE I.—Disturbances.

Year.	Disturbances at Kew.		Storms at Greenwich, after MAUNDER.
	Number of days.	Number of storms.	
1890	6	3	7
1891	22	12	14
1892	30	18	26
1893	11	7	20
1894	21	14	16
1895	19	14	11
1896	39	18	18
1897	14	11	11
1898	19	12	12
1899	20	11	12
1900	8	5	3
Total	209	125	150

§ 6. Table II. gives the distribution of the disturbances and disturbed days throughout the year, with corresponding data from Mr. MAUNDER's list; it also gives some particulars as to the amplitudes of the movements. In two cases, March–April, 1891, and January–February, 1896, where successive disturbed days belonged to two different months, the disturbance has been counted as two. In the second of these cases *six* successive days were treated as disturbed; no other sequence of disturbed days exceeded four. The Kew data in Table II. give a smoother annual distribution than the Greenwich data, and place the equinoctial maxima—which are prominent in both cases—somewhat later in the year. Both sets of figures make the spring maximum the more important. I have shown elsewhere that Mr. MAUNDER'S figures give a less accentuated annual inequality in years of many than in years of few sunspots. The same is true of the Kew data summarised in Table II. If we group the 34 disturbed days of 1890, 1899, and 1900, the years of fewest sunspots, and the 81 disturbed days of 1892 to 1895, the years of most sunspots, we find for the percentage number of occurrences in the three seasons, viz. :—

TABLE II.—Distribution of Disturbances.

Month.	MAUNDER'S storms at Greenwich.	Kew. Number of separate storms.	Number of days disturbed.	Mean range.	Largest range.	Number of disturbed days when range—			
						Over 60′.	Between 60′ and 40′.	Between 40′ and 20′.	Under 20′.
				′	′				
January .	12	10	22	26·5	49·2	0	1	17	4
February .	22	15	24	36·5	>79·0	2	6	16	0
March . .	21	19	30	34·0	85·6	3	4	19	4
April . .	12	11	17	29·5	58·0	0	1	13	3
May . .	14	9	16	36·5	77·4	1	6	9	0
June . .	7	5	6	35·3	40·5	0	2	4	0
July . .	8	7	10	38·3	77·0	2	2	4	2
August .	12	8	10	34·2	83·2	2	0	7	1
September.	16	10	15	33·8	57·7	0	3	11	1
October .	9	14	25	25·9	35·9	0	0	21	4
November.	10	10	20	33·3	53·9	0	3	17	0
December .	7	9	14	29·1	50·3	0	3	8	3

	Winter. (November to February.)	Equinox.	Summer. (May to August.)
Years of sunspot minimum . .	41	44	15
„ „ maximum . .	41	34	25

§ 7. The Kew disturbed days were got out without any reference whatsoever to Mr. MAUNDER'S list. It seems thus worth while considering whether they afford support or otherwise to his conclusion that magnetic storms tend to follow one another at an interval of about $27\frac{1}{4}$ days. Defining an "interval" as the time between the noons of the first days of two successive storms, the 110 intervals shorter than 60 days which were presented by the 125 storms at Kew were as follows :—

Interval	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Occurrences	5	6	4	4	4	0	1	3	0	5	2	2	3	6	1
Interval	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Occurrences	5	3	0	2	3	1	0	3	6	4	6	5	3	2	1
Interval	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46
Occurrences	3	0	0	0	0	1	1	2	0	1	0	2	2	1	0
Interval	47	48	49	50	51	52	53	54	55	56	57	58	59		
Occurrences	0	2	0	0	1	0	1	2	0	1	1	0	0		

The number of days in the remaining 14 intervals were respectively 62, 62, 64, 65, 76, 83, 87, 89, 93, 96, 100, 107, 112 and 272.

In the case of the two-day or even the three-day intervals, it might occasionally be questioned whether the successive storms should not have been counted as one, and conversely what was really one storm may occasionally have been counted as two.

Dividing the period between the first and last of the 125 storms by 124 we deduce 30·0 days as the average interval. If, however, we omit 1890 and 1900, years in which storms were very scarce, the average interval is reduced to 27·8. This should be borne in mind when considering the significance of the considerable number of times when the interval lay between 25 and 28 days.

§ 8. The disturbed days were not absolutely the only ones excluded from the computation of the regular diurnal variation. A very small number of days had to be excluded through stoppage of the clock or other misadventure. When only a few hours' trace had been lost during a quiet time, data were interpolated with the assistance of the Falmouth curves, kindly lent by Mr. Kitto.

With a view to the study of sunspot influence on the magnetic state of individual days, it was important to have a complete set of values of the absolute daily range (maximum less minimum). Stoppage of the clock—a rare occurrence—may conceal the exact time of the maximum or minimum, but it does not hide the extent of the range. In most cases of a short failure of trace one could be absolutely certain, having regard to the corresponding Falmouth curve, that neither maximum nor minimum was involved. But in a certain number of cases, especially in January during the determination of the scale values, there was some slight uncertainty, and in these cases the range was taken from the Falmouth curves. This raises no appreciable uncertainty, for, as I have shown elsewhere, declination amplitudes at Kew and Falmouth are practically identical. Only once during the whole 11 years —viz., on February 14, 1892—was there loss of trace owing to the light going beyond the edge of the sheet during a magnetic storm. In this case the maximum was taken as at the edge of the paper, so that the range deduced, 79′, is almost certainly an underestimate. This is, I think, the sole occasion during the whole 11 years in which there was any appreciable uncertainty as to the range.

Mean Annual Values.

§ 9. A question of interest is whether any sensible difference, systematic or otherwise, exists between mean yearly values derived from all *ordinary* ("undisturbed") days and from *quiet* days. In the case of Pawlowsk (St. Petersburg) MÜLLER[*] found that the mean annual values of the declination derived from WILD's "normal" days (which are very few in number and exceptionally quiet) were throughout the period 1873–85 invariably higher (more westerly) than those derived from all ordinary days, the average excess being 0′·24. Again, W. ELLIS[†] found for the seven years 1889–96 at Greenwich that the yearly means from the Astronomer Royal's quiet days were on the average 0′·08 higher than those from ordinary days. Only one year, 1891, showed the opposite phenomenon. Recently, however, ELLIS[‡] has found that while the quiet day mean was the larger in 1903 by 0′·1, it was smaller by the same amount in 1904.

To make the comparison absolutely fair, the mean quiet day in each month ought to come exactly in the middle of the month. This is only approximately true of the Astronomer Royal's quiet days. This being so, it seemed hardly worth while attempting an accuracy of the order 0′·01 in individual years, as this would have entailed the recalculation of the quiet day mean values, which are given in A only to the nearest 0′·1. Only the last seven years of the period were considered individually. The results obtained were as follows:—

ALGEBRAIC Excess of Quiet Day Mean.

1894.	1895.	1896.	1897.	1898.	1899.	1900.	Whole 11 years.
−0′·1	0′·0	+0′·1	+0′·1	+0′·1	0′·0	−0′·1	+0′·02

For Greenwich Mr. ELLIS, using the same quiet days, got +0′·1 in all three years 1894 to 1896.

Taking everything into account, all we seem entitled to infer is that the Astronomer Royal's quiet days give a yearly mean in very close agreement with that obtained when only days of marked disturbance are omitted.

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[*] 'Repertorium für Meteorologie,' vol. 12, No. 8, 1889.

[†] 'Brit. Assoc. Report for 1898,' p. 80 (see especially p. 108).

[‡] 'Roy. Soc. Proc.,' vol. 79, p. 15.

Diurnal Inequality.

§ 10. Tables III. and IV. give the mean diurnal inequalities for the several months of the year derived from the "ordinary" days (including the "quiet" days) and the "disturbed" days respectively. Non-cyclic changes have been eliminated in the usual way. The data in Table III. represent arithmetic means from the 11 months of the same name in the 11 years. All the ordinary day curves were smoothed, when necessary, as already described. In the case of the disturbed days the different

TABLE III.—Diurnal Inequality. Ordinary Days (+ to West).

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
	′	′	′	′	′	′	′	′	′	′	′	′
January	−1·24	−1·01	−0·80	−0·76	−0·72	**−0·70**	−0·74	**−0·85**	−0·63	+0·36	+1·61	+2·78
February	−1·74	−1·46	−1·34	−1·25	−1·24	−1·22	**−1·16**	**−1·26**	−1·17	−0·05	+1·78	+3·32
March	−1·75	**−1·68**	−1·70	−1·72	−1·75	−1·79	−2·27	**−3·02**	−2·76	−0·94	+2·02	+4·77
April	−1·42	−1·47	−1·63	−1·93	−2·19	−2·74	−3·64	**−4·22**	−3·53	−1·22	+2·04	+5·19
May	−1·38	−1·58	−1·86	−2·37	−3·26	−3·98	**−4·46**	−4·17	−2·85	−0·27	+2·76	+5·24
June	−1·24	−1·48	−1·88	−2·61	−3·71	−4·61	**−4·91**	−4·61	−3·39	−0·99	+2·00	+4·61
July	−1·28	−1·63	−1·93	−2·53	−3·68	−4·43	**−4·54**	−4·19	−3·07	−0·91	+1·90	+4·56
August	−1·66	−1·86	−2·13	−2·49	−3·19	−3·88	**−4·21**	−3·82	−2·30	+0·34	+3·29	+5·87
September	−1·88	−1·93	−2·10	−2·24	−2·35	−2·65	**−3·07**	−3·06	−1·85	+0·60	+3·46	+5·75
October	−1·62	−1·49	−1·41	**−1·31**	**−1·31**	−1·37	−1·72	**−2·40**	−2·27	−0·47	+2·45	+4·58
November	−1·31	−0·99	−0·81	**−0·78**	−0·79	−0·85	−0·85	**−1·12**	−1·11	+0·01	+1·76	+3·18
December	−1·18	−0·84	−0·66	−0·48	−0·47	**−0·46**	−0·49	−0·53	**−0·54**	+0·19	+1·32	+2·41

	Afternoon.												Range.	Sum of 24 differences from mean.
Hour . . .	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Midt.		
	′	′	′	′	′	′	′	′	′	′	′	′	′	′
January. . . .	**+3·26**	+2·66	+1·75	+1·23	+0·80	+0·30	−0·28	−0·88	−1·37	**−1·66**	−1·64	−1·49	4·92	29·52
February . . .	**+4·08**	+3·99	+3·01	+1·82	+1·12	+0·55	−0·04	−0·66	−1·33	−1·74	−1·96	**−1·98**	6·06	39·27
March	**+6·06**	+5·85	+4·41	+2·52	+0·99	+0·24	−0·34	−0·76	−1·24	−1·55	−1·68	**−1·80**	9·08	53·61
April.	**+6·73**	+6·40	+4·79	+3·05	+1·50	+0·31	−0·34	−0·71	−0·96	−1·26	−1·36	−1·40	10·95	60·03
May	**+6·20**	+5·86	+4·55	+3·07	+1·74	+0·62	−0·06	−0·38	−0·58	−0·77	−0·96	−1·16	10·66	60·13
June	+5·82	**+6·01**	+5·14	+3·81	+2·30	+1·17	+0·41	+0·10	−0·16	−0·32	−0·61	−0·93	10·92	62·82
July	+5·92	**+6·05**	+5·04	+3·52	+2·03	+0·93	+0·36	+0·10	−0·14	−0·38	−0·70	−0·98	10·59	60·80
August	**+6·80**	+6·19	+4·57	+2·54	+0·91	+0·02	−0·22	−0·44	−0·67	−0·98	−1·21	−1·45	11·01	61·04
September. . .	**+6·42**	+5·53	+3·81	+2·02	+0·73	+0·08	−0·36	−0·82	−1·16	−1·43	−1·69	−1·85	9·49	56·84
October. . . .	**+5·33**	+4·74	+3·48	+1·94	+0·94	+0·28	−0·37	−1·01	−1·52	−1·81	**−1·90**	−1·77	7·73	47·47
November . . .	**+3·61**	+3·06	+2·13	+1·47	+0·84	+0·27	−0·29	−0·89	−1·47	−1·73	**−1·76**	−1·63	5·37	32·71
December . . .	**+2·86**	+2·43	+1·77	+1·22	+0·67	+0·13	−0·42	−0·91	−1·37	**−1·60**	−1·58	−1·50	4·46	26·03

years were not treated independently, thus the results in Table IV. depend more on the years having many disturbed days than on those having few. No smoothing was applied to the disturbed curves, readings being simply taken exactly at the hours. Until the means were calculated, one could not but feel doubtful whether a diurnal inequality would be recognisable, thus the comparative smoothness of the results is not a little remarkable.

TABLE IV.—Diurnal Inequality Disturbed Days (+ to West).

	Forenoon.											
Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
	′	′	′	′	′	′	′	′	′	′	′	′
January	− **6·02**	−2·77	−2·82	+0·27	+0·66	+0·73	+1·37	+0·97	+1·22	+2·19	+3·25	+4·31
February	− 3·51	−**5·03**	−3·89	−1·65	−0·56	+1·77	+0·38	+0·91	+1·18	+1·51	+3·54	+4·15
March	− 4·50	−3·89	−6·15	−3·23	−0·40	−1·01	−0·50	−0·38	−0·22	+2·15	+4·76	+6·97
April	− 5·28	−5·36	−4·42	−3·92	−4·25	−2·77	−2·57	−2·74	−0·28	+2·27	+5·27	+8·51
May	− 6·35	−6·23	−5·95	−2·92	−1·86	−2·69	−2·14	−2·77	−1·54	+1·15	+5·36	+6·37
June	−**10·12**	−6·91	−6·15	−3·79	−1·90	+0·49	−1·58	−3·15	−0·66	+1·90	+4·64	+6·80
July	− **5·51**	−3·13	−4·98	−3·04	+1·76	−2·86	−4·53	−2·71	−2·28	−0·71	+1·77	+6·28
August	− 4·19	−3·87	−0·64	−0·99	+0·96	−1·04	+1·23	−1·71	−1·64	−0·29	+1·41	+5·91
September	− 3·59	−4·33	−2·74	−1·07	−1·44	−0·98	−1·21	−0·43	+0·81	+2·72	+5·86	+7·90
October	− 2·01	−1·47	−1·56	−0·68	+0·17	+0·61	+0·25	−0·17	+0·78	+2·79	+4·57	+6·36
November	− 3·08	−1·78	−0·66	0·00	+1·94	+1·59	+4·05	+1·50	+1·47	+2·67	+3·92	+**5·82**
December	− 4·00	−3·53	−2·67	−2·63	−0·40	+0·44	+0·47	+1·01	+0·52	+2·07	+1·60	+3·98

	Afternoon.												Range.	Sum of 24 differences from mean.
Hour . . .	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Midt.		
	′	′	′	′	′	′	′	′	·	′	′	′	′	′
January . . .	+ 4·35	+ **4·88**	+3·80	+3·00	+0·97	+0·59	+0·03	−2·41	−5·26	−4·77	−5·11	−3·41	10·90	65·16
February . . .	+ **6·02**	+ 5·83	+5·78	+3·89	+0·97	−2·34	−1·99	−1·36	−4·40	−3·37	−4·12	−3·60	11·05	71·75
March	+ 8·64	+ **8·74**	+8·08	+5·23	+3·03	+1·32	−2·78	−4·85	−5·21	−**6·21**	−4·60	−4·90	14·95	97·75
April	+10·68	+**10·75**	+8·49	+5·83	+4·04	+1·62	−1·93	−**5·85**	−4·40	−4·13	−4·58	−4·95	16·60	114·89
May	+ **8·98**	+ 7·92	+7·83	+6·97	+5·50	+2·21	+0·68	−1·65	−4·54	−1·38	−**6·72**	−6·26	15·70	105·97
June	+ 6·95	+ **7·22**	+5·85	+3·49	+3·60	+1·63	+0·61	−0·08	−0·86	+2·94	−6·10	−4·82	17·34	92·24
July	+ 6·86	+ **7·73**	+7·20	+4·55	+3·45	+2·52	+2·21	−2·31	−3·09	−2·69	−2·46	−4·08	13·24	88·71
August	+ 7·24	+ **7·58**	+6·71	+5·10	+2·75	+0·25	−2·47	−**7·04**	−2·86	−4·89	−4·80	−2·73	14·62	78·30
September . . .	+ **8·50**	+ 7·86	+4·86	+2·93	+2·50	−1·92	−3·27	−**5·92**	−5·12	−5·56	−4·52	−1·72	14·42	87·76
October	+ **6·81**	+ 6·52	+4·25	+1·34	+0·48	−1·03	−4·62	−5·48	−4·90	−**6·11**	−4·26	−2·67	12·92	69·89
November . . .	+ 4·98	+ 4·98	+2·82	+2·71	+0·19	−1·39	−4·21	−4·04	−**6·56**	−5·57	−6·52	−4·74	12·38	77·19
December . . .	+ 4·45	+ **5·33**	+3·65	+3·30	+4·09	+0·92	+0·74	−0·44	−**6·55**	−4·76	−4·88	−2·80	11·88	65·23

Tables similar to III. were also formed for the years of sunspot maximum (1892 to 1895) and of sunspot minimum (1890, 1899, and 1900) independently, but these are omitted here. Table V. contains, however, diurnal inequalities calculated from the whole year and the three seasons, viz., winter (November to February), summer (May to August), and equinox.

TABLE V.—Diurnal Inequality. Ordinary Days.

Season.		Forenoon.											
	Hour	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
		′	′	′	′	′	′	′	′	′	′	′	′
Year . .	Sunspot minimum . . .	−1·08	**−1·01**	−1·08	−1·29	−1·62	−1·92	−2·21	**−2·31**	−1·75	−0·16	+1·96	+3·78
	11 years.	−1·48	**−1·45**	−1·52	−1·71	−2·06	−2·39	−2·67	**−2·77**	−2·12	−0·28	+2·20	+4·35
	Sunspot maximum . .	−1·84	−1·90	−1·98	−2·17	−2·54	−2·93	−3·23	**−3·31**	−2·57	−0·44	+2·42	+4·97
Winter .	Sunspot minimum . . .	−0·90	−0·64	−0·52	**−0·51**	−0·52	−0·55	−0·59	**−0·69**	−0·58	+0·30	+1·57	+2·54
	11 years.	−1·37	−1·07	−0·90	−0·82	−0·81	**−0·81**	−0·81	**−0·94**	−0·86	+0·13	+1·62	+2·92
	Sunspot maximum . .	−1·79	−1·50	−1·29	−1·16	−1·10	**−1·09**	−1·09	**−1·28**	−1·27	−0·09	+1·72	+3·36
Equinox .	Sunspot minimum . . .	−1·24	**−1·13**	−1·27	−1·37	−1·47	−1·66	−2·17	**−2·75**	−2·30	−0·50	+2·08	+4·34
	11 years.	−1·67	**−1·64**	−1·71	−1·80	−1·90	−2·14	−2·67	**−3·18**	−2·60	−0·51	+2·49	+5·07
	Sunspot maximum . .	−2·05	−2·13	−2·20	−2·28	−2·39	−2·70	−3·26	**−3·73**	−3·05	−0·65	+2·76	+5·72
Summer .	Sunspot minimum . . .	−1·09	−1·25	−1·46	−1·99	−2·87	−3·54	**−3·87**	−3·48	−2·37	−0·27	+2·24	+4·45
	11 years.	−1·39	−1·64	−1·95	−2·50	−3·46	−4·22	**−4·53**	−4·20	−2·90	−0·46	+2·49	+5·07
	Sunspot maximum . .	−1·68	−2·05	−2·45	−3·06	−4·12	−5·01	**−5·33**	−4·91	−3·40	−0·59	+2·75	+5·82

Season.		Afternoon.												Range.	Sum of 24 differences from mean.
	Hour . . .	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	Midt.		
		′	′	′	′	′	′	′	′	′	′	′	′	′	′
Year .	Sunspot minimum	**+4·44**	+3·93	+2·75	+1·58	+0·71	+0·17	−0·20	−0·53	−0·84	−1·05	**−1·15**	−1·14	6·75	38·66
	11 years	**+5·26**	+4·90	+3·70	+2·35	+1·21	+0·41	−0·16	−0·60	−1·00	−1·27	−1·42	**−1·50**	8·03	48·78
	Sunspot maximum	**+6·13**	+5·91	+4·62	+3·05	+1·64	+0·65	−0·06	−0·62	−1·06	−1·37	−1·61	−1·77	9·44	58·79
Winter	Sunspot minimum	**+2·83**	+2·19	+1·27	+0·70	+0·39	+0·02	−0·38	−0·77	−1·21	**−1·38**	−1·36	−1·20	4·21	23·61
	11 years	**+3·45**	+3·03	+2·17	+1·43	+0·86	+0·31	−0·26	−0·84	−1·38	−1·68	**−1·73**	−1·65	5·18	31·85
	Sunspot maximum	**+4·10**	+3·89	+2·98	+2·04	+1·23	+0·61	−0·10	−0·84	−1·47	−1·85	**−2·01**	−2·00	6·11	39·86
Equinox	Sunspot minimum	**+5·19**	+4·54	+3·10	+1·57	+0·55	+0·08	−0·26	−0·62	−0·94	−1·18	−1·31	**−1·32**	7·94	42·94
	11 years	**+6·14**	+5·63	+4·12	+2·38	+1·04	+0·23	−0·35	−0·82	−1·22	−1·51	−1·66	**−1·71**	9·32	54·19
	Sunspot maximum	**+7·10**	+6·71	+5·10	+3·17	+1·51	+0·46	−0·31	−0·88	−1·34	−1·65	−1·87	−2·00	10·83	65·02
Summer	Sunspot minimum	**+5·29**	+5·06	+3·89	+2·46	+1·20	+0·42	+0·04	−0·20	−0·36	−0·59	−0·77	−0·90	9·16	50·06
	11 years	**+6·18**	+6·03	+4·82	+3·23	+1·74	+0·68	+0·12	−0·15	−0·39	−0·61	−0·87	−1·13	10·71	60·76
	Sunspot maximum	**+7·19**	+7·13	+5·78	+3·95	+2·19	+0·88	+0·22	−0·13	−0·36	−0·60	−0·95	−1·31	12·52	71·89

All maximum and minimum values which are distinctly shown appear in heavy type in Tables III. and V.; but in Table IV. only the absolutely largest and least values are thus indicated.

In the case of the ordinary days a double daily period is always clearly apparent in winter; but this tends to disappear in the equinoctial months, especially in years of sunspot maximum, and it is not recognisable in summer, even in the years of sunspot minimum.

§ 11. Table VI. gives the range of the diurnal inequality on ordinary days—still from hourly readings—for each individual month of the eleven years. It is instructive to compare the monthly means in Table VI. with the corresponding ranges in Tables III. and V. The observational data are exactly the same, and at first sight it may appear strange that the mean ranges in Table VI. are as a rule not equal to but greater than the ranges in Table III. This is due simply to the fact that the hours of maxima and minima vary slightly from year to year. The greater this variation the more does the mean in Table VI. exceed that in Table III. On the average of the 12 months the mean range in Table VI. is almost exactly 1 per cent. greater than that in Table III., but the ratio of the two ranges is notably largest in winter, varying from 1·03 in January to 1·00 in April, June and August.

TABLE VI.—Diurnal Inequality Ranges from Ordinary Days.

	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Yearly means.
	′	′	′	′	′	′	′	′	′	′	′	′	′
1890	4·40	5·11	7·94	9·66	8·56	9·10	8·82	9·44	8·61	6·93	5·28	3·94	7·32
1891	4·27	5·07	8·36	10·35	11·37	9·99	11·23	10·85	9·69	9·13	6·83	4·64	8·48
1892	6·02	8·09	10·79	11·88	11·96	12·15	11·92	12·67	10·60	9·99	6·01	6·10	9·85
1893	5·90	7·99	11·84	14·40	13·31	13·87	13·05	14·36	12·09	9·97	6·66	5·39	10·74
1894	5·70	7·67	10·47	12·97	12·43	11·92	12·11	12·90	11·22	8·87	6·26	5·06	9·80
1895	5·60	7·40	9·56	12·57	12·73	14·11	12·66	10·71	9·85	7·78	6·16	5·38	9·54
1896	6·24	7·55	10·11	11·30	9·79	10·06	10·52	10·90	9·89	6·76	4·68	4·21	8·50
1897	4·54	5·39	8·88	10·23	9·88	9·68	9·62	10·27	8·52	6·48	5·36	4·22	7·76
1898	4·58	5·49	7·83	9·02	9·90	10·15	9·64	9·84	8·33	7·08	4·99	4·22	7·59
1899	4·16	4·73	7·54	9·46	9·40	9·88	8·53	9·72	9·16	6·71	4·49	3·80	7·30
1900	4·14	4·61	7·15	8·64	8·44	9·40	9·15	9·52	7·66	6·52	3·53	3·25	6·83
Monthly means	5·05	6·28	9·13	10·95	10·71	10·94	10·66	11·02	9·60	7·84	5·48	4·56	8·52

If we compare the arithmetic mean of the 132 ranges of Table VI. with the range in the mean diurnal inequality for the year in Table V. from the 11-year period, we find that the former is 6 per cent. the larger. This shows that the variability with the season of the year in the hours of maximum and minimum is greater than is the variability for the same month of the year in different years.

§ 12. Fig. 1 shows the mean diurnal inequalities for the year from the 11-year period for the ordinary and the disturbed days, with, for comparison, the corresponding inequality derived in A from quiet days. The difference between the ordinary and quiet day curves, though not large, is systematic.

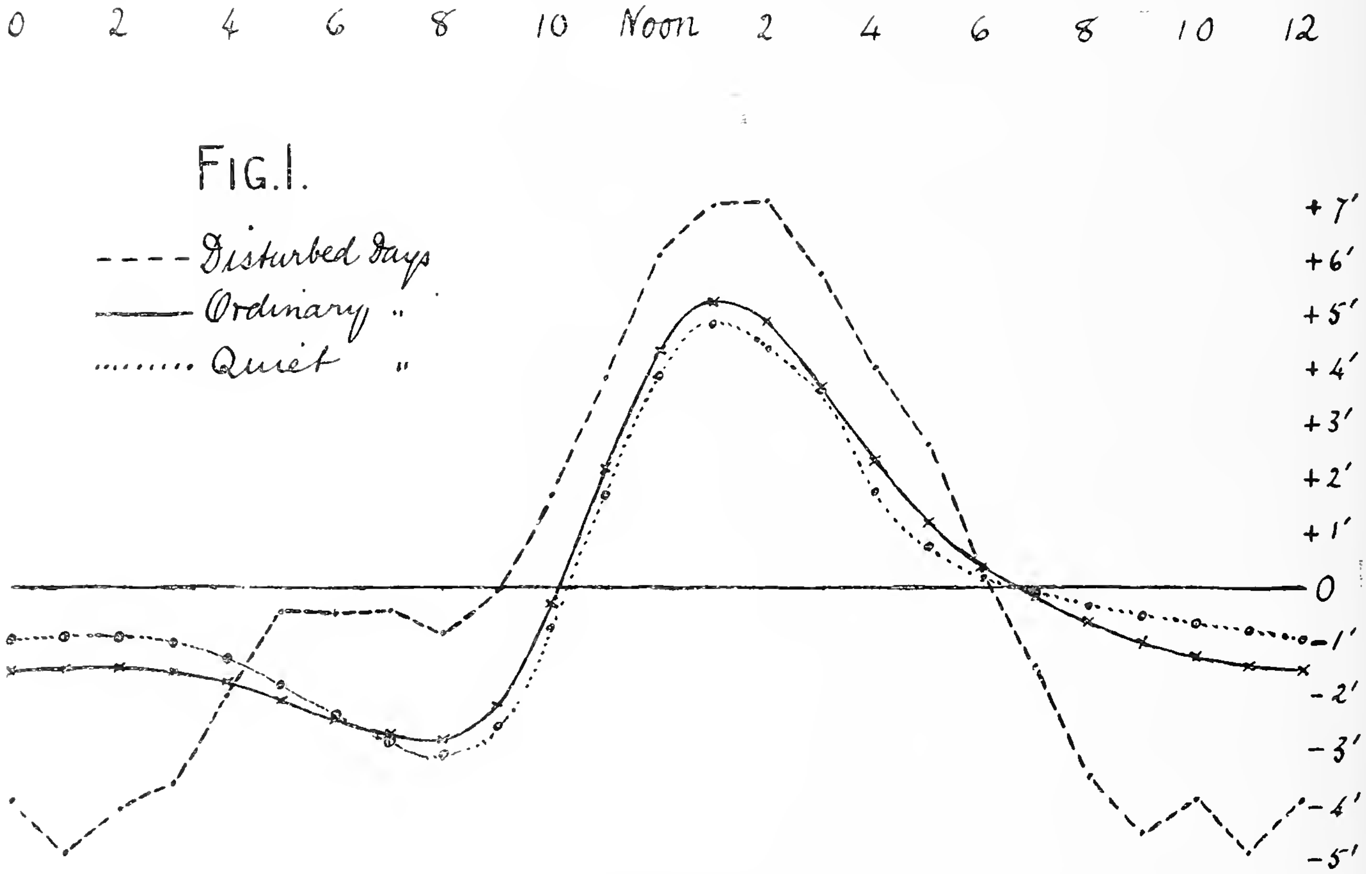

FIG. I.

The curves of fig. 2 represent the *differences* between the diurnal inequalities in years of sunspot maximum and minimum, and between the inequalities in ordinary and quiet days for the year as a whole and the three seasons. The ordinates represent the excess in the westerly declination in years of sunspot maximum (or in ordinary days) over the declination at the same hour in years of sunspot minimum (or in quiet days). The difference curves for sunspot maximum and minimum are of the same general type as ordinary inequality curves; but the difference curves for ordinary and quiet days are of a totally distinct character. These latter curves are double peaked in equinox and summer, but show only one distinct maximum and minimum in winter.

Fig. 3 gives difference curves in the case of the mean diurnal inequality for the whole year from disturbed, ordinary, and quiet day curves. The difference curves involving the disturbed days display a remarkably sudden rise and fall and are comparatively flat topped from 5 a.m. to 5 p.m. Disturbed and quiet days difference curves (not reproduced here) for winter, equinox, and summer all show this rapid rise and fall, and they are all fairly symmetrical with reference to the ordinate for noon. The summer curve has two well-marked maxima, with a secondary minimum near noon; even in the equinox the depression near noon is distinctly visible.

The amplitude of the diurnal inequality varies so much that it is difficult to recognise the difference in type between curves for the different seasons when drawn on the same scale. Fig. 4 shows the inequalities for the three seasons on different scales, so related that the mean of the 24-hourly ordinates is the same for each. This brings out very clearly the fact that the difference in type is mainly between 7 p.m. and 9 a.m., *i.e.*, during the hours when the diurnal movement is least conspicuous.

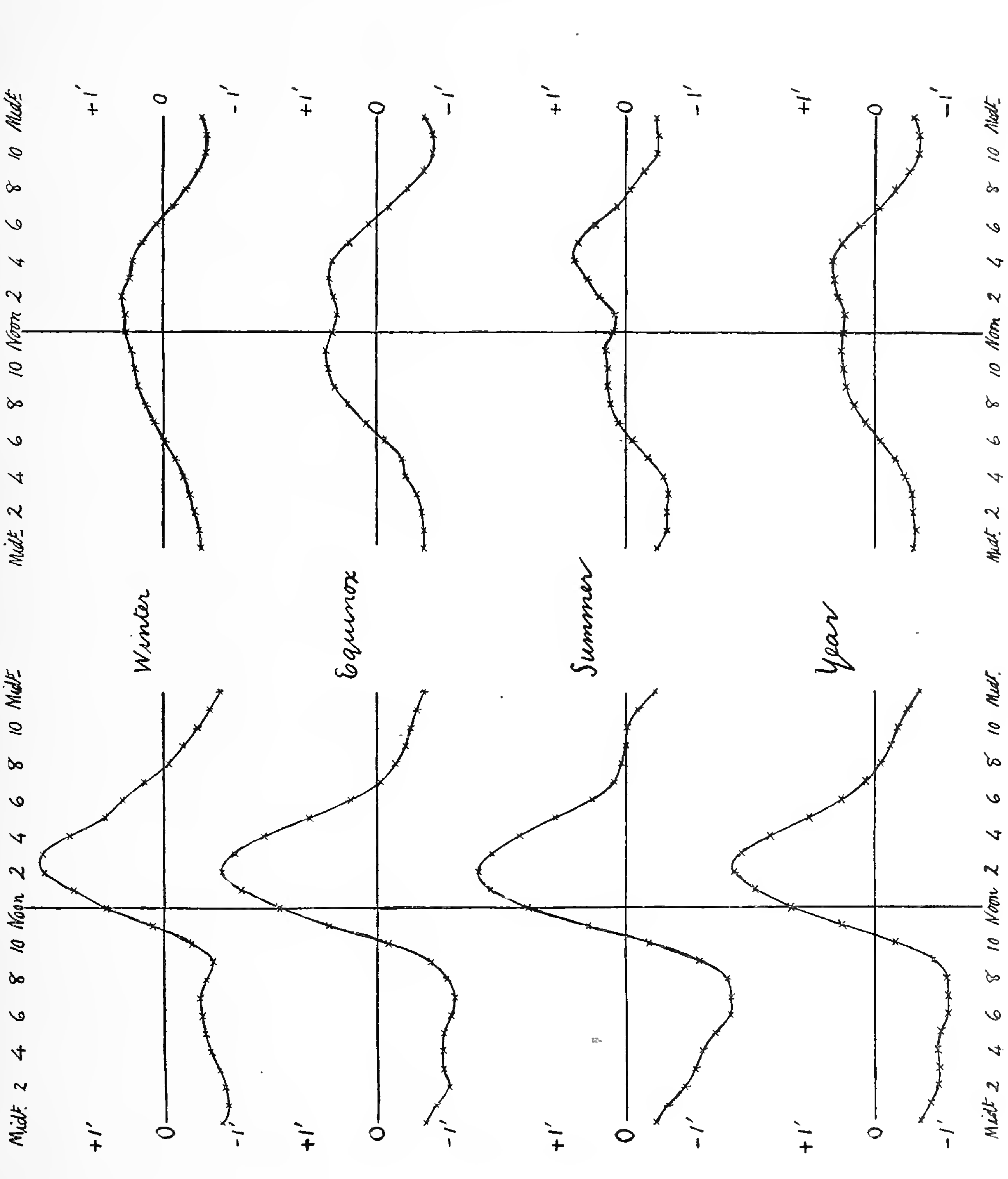

FIG. 2. Ordinary Days less Quiet Days 1890 to 1900.

Ordinary Days 1892–95 less 1890, 1899, 1900.

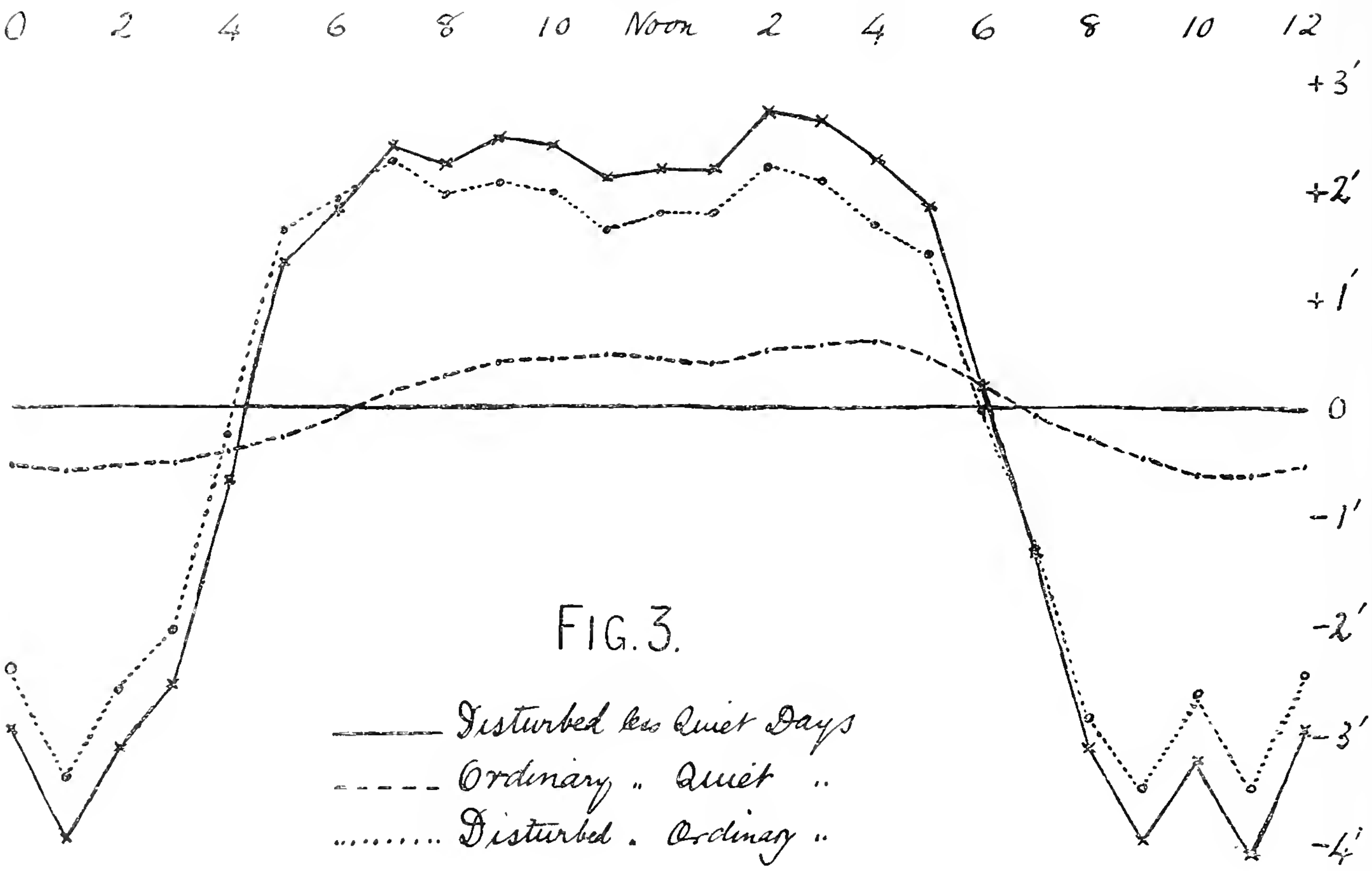
FIG. 3.
0
2
4
6
8
10
Noon
2
4
6
8
10
12
+3′
+2′
+1′
0
-1′
-2′
-3′
-4′
Disturbed less Quiet Days
Ordinary " Quiet "
Disturbed " Ordinary "

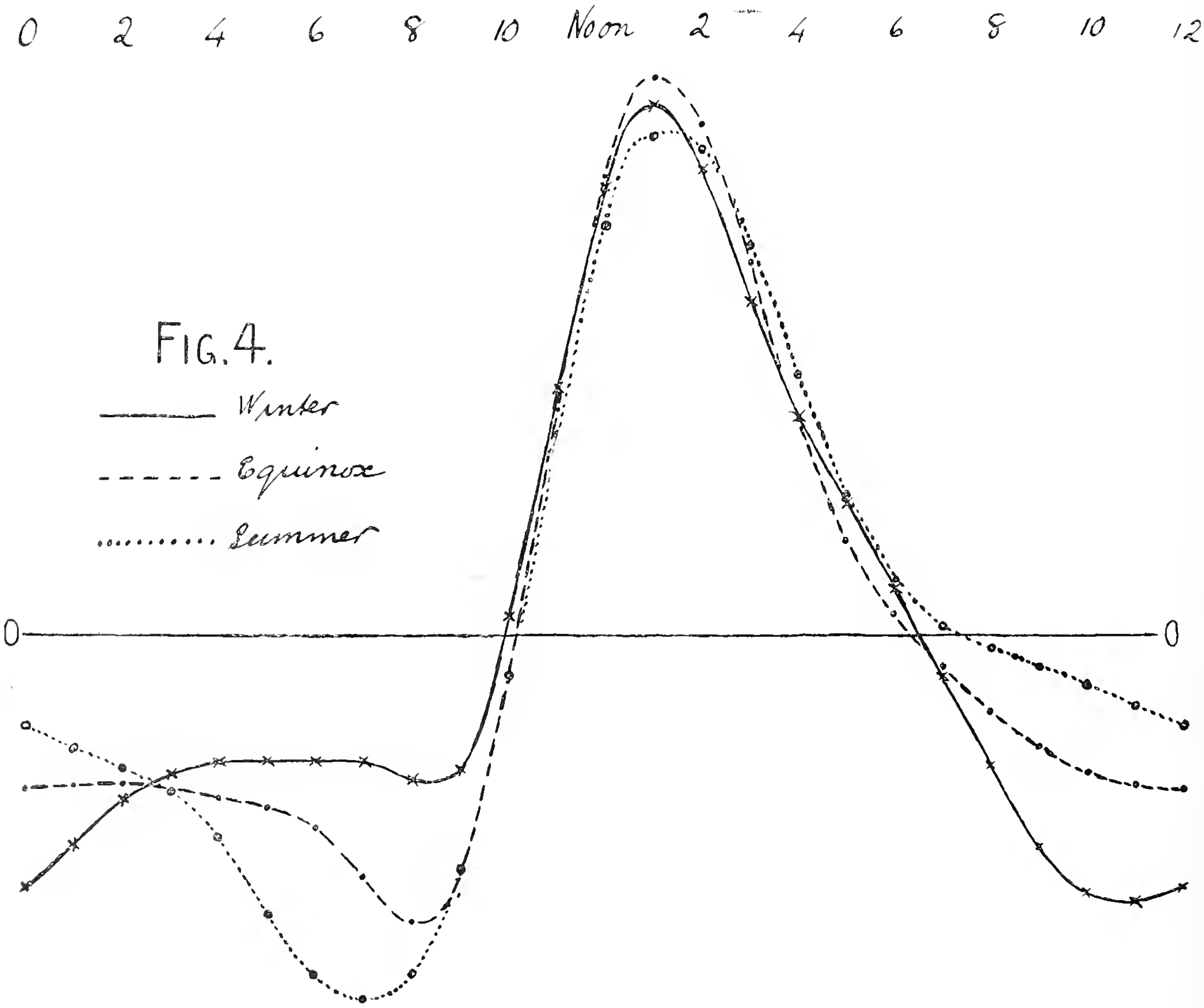
FIG. 4.
0
2
4
6
8
10
Noon
2
4
6
8
10
12
0
0
Winter
Equinox
Summer

Diurnal Inequality. Fourier Coefficients.

§ 13. The diurnal inequality was analysed in the usual way in a series

$$c_1 \sin(t+\alpha_1) + c_2 \sin(2t+\alpha_2) + \ldots,$$

where t is time counted from midnight (G.M.T.), one hour being taken as equivalent to 15°. Thus c_1, c_2, c_3, c_4, denote the amplitudes, α_1, α_2, α_3, and α_4 the phase angles of the terms whose periods are respectively 24, 12, 8, and 6 hours. The object of such an analysis is to provide a ready means of tracing affinities and differences between different stations at the same season, and between different seasons at the same station. The most instructive way of presenting the facts is probably to show side by side the corresponding results for the different types of years and for the different kinds of days.

Table VII. contrasts the amplitudes of the 24- and 12-hour terms from ordinary and disturbed days for each month of the year. Similar complete results were calculated for the 8- and 6-hour terms, but only those for ordinary days from the 11-year period are included. A complete set of seasonal values are, however, given

TABLE VII.—Diurnal Inequality. Fourier Coefficients. Amplitudes.

	c_1.				c_2.				c_3.	c_4.
	Ordinary days.			Disturbed days.	Ordinary days.			Disturbed days.	Ordinary days.	Ordinary days.
	Sun-spot minimum.	11 years.	Sun-spot maximum.	11 years.	Sun-spot minimum.	11 years.	Sun-spot maximum.	11 years.	11 years.	11 years.
	′	′	′	′	′	′	′	′	′	′
January . . .	1·44	1·79	2·17	4·27	0·66	0·86	1·03	1·27	0·41	0·27
February . . .	1·73	2·41	3·17	4·49	0·84	1·11	1·35	1·25	0·57	0·30
March. . . .	2·25	3·05	3·73	6·26	1·65	1·98	2·32	2·29	1·11	0·45
April	2·61	3·35	4·06	7·03	2·08	2·48	2·91	2·87	1·17	0·39
May	2·81	3·57	4·36	6·73	2·00	2·38	2·75	1·79	0·87	0·17
June	3·19	3·83	4·62	5·89	2·18	2·39	2·81	0·05	0·74	0·05
July	2·97	3·72	4·45	5·01	1·95	2·30	2·61	2·09	0·77	0·11
August . . .	3·06	3·64	4·15	4·47	2·14	2·43	2·79	2·94	1·05	0·18
September . .	2·74	3·35	3·94	5·42	1·74	2·02	2·27	2·58	1·04	0·35
October . . .	2·09	2·69	3·39	4·55	1·42	1·69	1·92	2·38	0·92	0·48
November . .	1·44	1·94	2·28	4·90	0·88	1·06	1·30	1·71	0·51	0·32
December. . .	1·14	1·61	2·06	4·17	0·75	0·81	0·94	1·35	0·35	0·20
Arithmetic means .	2·29	2·91	3·53	5·27	1·52	1·79	2·08	1·88	0·79	0·27

in Table VIII., including data for quiet days. The great difference between different years and between days of different type cannot be brought too clearly home to those combining data from different stations for theoretical purposes. It will be noticed that c_1 increases regularly as we pass from years of sunspot minimum through average years to years of sunspot maximum, or as we pass from quiet days through ordinary to disturbed days. But c_2, whilst increasing with sunspot frequency, seems practically no larger in ordinary or even in disturbed days than in quiet days.

TABLE VIII.—Diurnal Inequality. Fourier Coefficients. Amplitudes.

	Season.	Quiet days.			Ordinary days.			Disturbed days.
		Sunspot minimum.	11 years.	Sunspot maximum.	Sunspot minimum.	11 years.	Sunspot maximum.	11 years.
		′	′	′	′	′	′	′
c_1	Year	1·80	2·32	2·86	2·21	2·84	3·47	5·07
	Winter	0·99	1·39	1·83	1·43	1·93	2·42	4·36
	Equinox	1·98	2·48	2·99	2·41	3·10	3·76	5·70
	Summer	2·56	3·19	3·85	2·98	3·67	4·38	5·46
c_2	Year	1·54	1·79	2·11	1·51	1·76	2·04	1·76
	Winter	0·75	0·91	1·12	0·78	0·96	1·15	1·34
	Equinox	1·74	2·01	2·34	1·71	2·02	2·33	2·50
	Summer	2·16	2·50	2·95	2·06	2·37	2·73	1·71
c_3	Year	0·79	0·89	1·01	0·72	0·78	0·89	0·80
	Winter	0·44	0·50	0·58	0·42	0·45	0·55	0·44
	Equinox	1·06	1·17	1·33	0·97	1·05	1·16	0·63
	Summer	0·90	1·01	1·14	0·77	0·85	0·97	1·38
c_4	Year	0·28	0·28	0·29	0·27	0·29	0·28	0·50
	Winter	0·25	0·26	0·30	0·27	0·27	0·30	0·43
	Equinox	0·45	0·47	0·46	0·42	0·41	0·42	1·15
	Summer	0·15	0·12	0·11	0·11	0·11	0·11	0·64

The influence of disturbance on c_3 seems very small. The values of c_4 seem almost independent of sunspot frequency, and those derived from ordinary and from quiet days are nearly equal.

The fact that c_2, c_3 and c_4 are so nearly the same for ordinary and quiet days may seem at first sight to imply that the ordinary and quiet day difference curve is necessarily almost a pure sine curve of 24-hour period. This conclusion, however, does not necessarily follow unless the phase angles are nearly the same in the two cases.

Diurnal Inequality. Phase Angles.

§ 14. Tables IX., X., and XI. contrast the phase angles for different species of days and for years of sunspot maximum (1892 and 1895) and minimum (1890, 1899, 1900).

TABLE IX.—Diurnal Inequality, 24-hour term. Phase Angle.

	Quiet days.			Ordinary days.			Disturbed days.
	1892–95.	1890–1900.	1890, 1899, 1900.	1892–95.	1890–1900.	1890, 1899, 1900.	1890–1900.
	° ′	° ′	° ′	° ′	° ′	° ′	° ′
January . . .	240 4	242 40	245 11	245 5	250 51	257 56	270 49
February . . .	232 9	233 38	240 50	237 9	241 44	249 15	265 27
March	222 24	224 55	228 47	232 17	232 52	233 47	257 17
April	209 35	213 26	217 42	222 1	224 30	223 35	248 9
May	217 7	216 47	217 58	219 57	221 2	224 10	241 30
June	206 55	207 24	202 39	212 46	212 15	212 8	240 15
July	210 35	210 58	211 20	214 32	214 18	215 12	234 26
August	221 26	224 55	227 51	225 6	227 53	229 12	260 6
September . . .	227 46	229 2	229 41	234 5	236 37	237 23	267 12
October . . .	227 40	227 12	224 21	236 32	239 48	239 52	279 46
November . . .	232 14	240 26	251 24	242 29	248 1	254 51	289 33
December . . .	239 53	251 53	261 50	248 37	254 47	263 35	258 32

TABLE X.—Diurnal Inequality, 12-hour term. Phase Angle.

	Quiet days.			Ordinary days.			Disturbed days.
	1892–95.	1890–1900.	1890, 1899, 1900.	1892–95.	1890–1900.	1890, 1899, 1900.	1890–1900.
	° ′	° ′	° ′	° ′	° ′	° ′	° ′
January . . .	20 35	27 43	36 25	22 50	29 13	44 45	− 28 28
February . . .	30 25	31 3	34 52	26 7	27 6	33 16	9 11
March	35 21	37 12	45 15	34 14	35 29	38 24	17 2
April	37 48	38 0	41 47	38 23	38 36	40 55	33 48
May	52 8	55 3	61 14	49 44	50 12	54 13	1 55
June	46 58	47 23	43 20	46 29	46 1	44 55	− 54 54
July	46 20	49 0	52 20	47 12	47 26	48 50	6 46
August	57 15	57 52	63 47	56 21	56 32	59 37	5 5
September . . .	55 32	57 27	62 3	53 38	54 38	56 49	40 19
October . . .	33 13	35 34	34 13	33 21	34 57	35 47	31 55
November . . .	24 29	33 33	50 39	23 9	27 39	38 14	− 3 49
December . . .	28 4	27 54	37 5	17 32	21 20	29 53	− 29 25

For purposes of comparison they reproduce some data for quiet days already published in A. It should be noticed that G.M.T. is used throughout. If local mean time were substituted, the angles would require to be increased, α_1 by 19′, α_2 by 38′, and so on. The corrections necessary if local solar time is employed will be found in A, Table XIX.

It should be remembered that an increase in phase angle implies an earlier occurrence of the daily maximum, an advance of one hour answering to 15° in α_1, to 30° in α_2, and so on.

Table XI.—Diurnal Inequality. Phase Angles.

Angle.	Season.	Quiet days.			Ordinary days.			Disturbed days.
		Sunspot maximum.	11 years.	Sunspot minimum.	Sunspot maximum.	11 years.	Sunspot minimum.	11 years.
		° ′	° ′	° ′	° ′	° ′	° ′	° ′
α_1	Year. . .	221 1	222 57	224 14	238 12	230 21	232 6	257 52
	Winter . .	235 36	240 55	248 49	242 38	248 8	255 40	271 42
	Equinox .	221 27	223 24	224 51	230 57	233 8	233 22	261 12
	Summer .	213 47	214 49	214 30	217 54	218 45	220 2	243 16
α_2	Year. . .	42 57	45 3	49 33	41 15	42 28	45 58	12 26
	Winter . .	26 3	30 18	40 25	22 50	26 31	36 17	– 12 43
	Equinox .	40 59	42 25	46 24	39 58	41 2	43 14	31 16
	Summer .	50 50	52 27	55 13	49 58	50 6	51 53	4 27
α_3	Year. . .	234 41	237 16	241 45	231 37	236 38	242 39	200 11
	Winter . .	236 7	243 14	255 10	233 0	243 19	256 37	188 35
	Equinox .	229 5	231 11	233 51	227 29	231 17	235 14	186 9
	Summer .	240 29	241 26	244 29	235 51	239 35	244 28	210 15
α_4	Year. . .	52 13	56 8	59 25	56 46	57 20	56 1	105 0
	Winter . .	49 25	55 19	64 22	51 4	53 54	59 35	65 50
	Equinox .	57 17	60 45	59 25	60 46	59 44	56 59	147 12
	Summer .	37 55	39 52	51 45	56 10	56 1	43 55	136 54

§ 15. The phenomenon to which I called attention in the case of the quiet days, viz., the increase in the phase angles α_1 and α_2 as sunspot frequency diminishes, appears equally decisively in the ordinary days. Turning the difference of angle into time, and taking arithmetic means from the individual months, we find for the retardation (in minutes) in the time of occurrence of the maxima in years of sunspot maximum, as compared to years of sunspot minimum, the following results, *q* denoting quiet, *o* all ordinary days :—

	Whole year.		Winter.		Equinox.		Summer.	
	q.	*o.*	*q.*	*o.*	*q.*	*o.*	*q.*	*o.*
24-hour term	24·0	23·5	54·9	52·3	13·5	9·7	3·7	8·3
12-hour term	15·8	12·8	27·7	28·2	10·7	6·2	9·0	3·9

§ 16. Contrasting results from ordinary and quiet days, we observe one remarkable difference between the 24- and 12-hour phase angles. As we pass from quiet to ordinary days the angle α_1 *invariably* increases, whereas in a majority of months α_2 decreases.

TABLE XII. converts the difference between the ordinary and quiet day phase angles into time. The results are from the seasonal diurnal inequalities, not from individual months.

TABLE XII.—Difference in Minutes in Times of Occurrence of Maxima in Ordinary and in Quiet Days (+ denoting Later Occurrence in Quiet Days).

	Whole year.		Winter.		Equinox.		Summer.	
	24-hour. +	12-hour. −	24-hour. +	12-hour. −	24-hour. +	12-hour. −	24-hour. +	12-hour. −
Years of sunspot maximum . .	27·6	3·2	29·0	7·0	37·5	1·2	16·4	1·5
Eleven years	27·2	4·8	26·8	7·5	39·8	2·3	15·4	4·6
Years of sunspot minimum . .	27·2	6·2	26·6	6·4	34·1	5·7	20·9	6·6

In the case of the 24-hour term the difference in phase between quiet and ordinary days seems nearly independent of sunspot frequency. Like the difference in phase between years of sunspot maximum and minimum, it is distinctly least in summer; but unlike that difference it is greater in the equinoctial than in the winter months.

In the case of α_3 and α_4 the difference between ordinary and quiet days appears small, and it would probably require a very long series of years to give thoroughly representative results. This last remark also applies to the difference between disturbed and ordinary days, though in this case there seems no doubt as to the sign of the difference.

§ 17. Table XIII. converts the difference between the disturbed and ordinary days phase angles into time. The results are again from the seasonal inequalities.

The differences in Table XIII. are very substantial. From Tables XII. and XIII., or directly from Table XI., we see that, taking the whole year, the maximum in the 24-hour term occurs no less than $2\frac{1}{4}$ *hours* earlier in disturbed than in quiet days.

Table XIII.—Difference in Minutes in Times of Occurrence of Maxima in Ordinary and Disturbed Days (+ denoting Later Occurrence in Ordinary Days).

	Whole year.	Winter.	Equinox.	Summer.
	h. m.	h. m.	h. m.	h. m.
24-hour term	+1 50	+1 44	+1 52	+1 38
12-hour „	−1 0	−1 18	−0 20	−1 31
8-hour „	−0 49	−1 13	−1 0	−0 39
6-hour „	+0 48	+0 12	+1 27	+1 21

We see how, as it were, by filtering out disturbed days we obtain a gradual retardation in the phase. Some of the Astronomer Royal's quiet days are decidedly less quiet than others. Supposing we adopted a still higher standard should we observe even more retardation? On the other hand, our disturbed days vary much in the degree of disturbance, and very considerably in its type. Is there an advance in phase irrespective of the type of disturbance, and is the advance greater in highly disturbed than in moderately disturbed days? Obviously there are many further questions arising out of the above result. Evidently a study of the phase constitutes a method of considerable delicacy for advancing our knowledge of disturbances; but a very obvious consideration is that in order to obtain even approximately smooth diurnal inequalities from highly disturbed days one must deal with a long period of years. When diurnal inequalities are not smooth, merely "accidental" irregularities may introduce a fictitious element into the Fourier coefficients, especially those of shorter period.

The results reached emphasise one difficulty in the way of an exact intercomparison of stations. Even if all stations suffered equally from disturbance, their published data would not be strictly comparable unless the standard for omitting disturbed days when forming the diurnal inequality were absolutely uniform. Under existing conditions all that we do know is that the standard is not uniform, and that there is no obvious way of making it so, whilst there is every reason to believe that the incidence of disturbance is widely different.

We have already referred to the different effects produced by disturbance in the angles α_1 and α_2. Possibly this difference may be connected in some way with another, viz., that whereas α_1 increases as we pass from summer to winter, α_2 diminishes. Summarising the results we have in short:—

α_1 largest in disturbed days, in winter, in years of sunspot minimum.
α_1 least in quiet days, in summer, in years of sunspot maximum.
α_2 largest in quiet days, in summer, in years of sunspot minimum.
α_2 least in disturbed days, in winter, in days of sunspot maximum.

Absolute Ranges.

§ 18. The regular diurnal inequality is of special interest for theorists, particularly those whose ambition it is to discover an explanation of the phenomena of terrestrial magnetism. There are, however, other facts connected with the daily changes which merit a close study. If we take the case of a surveyor or explorer making frequent use of an accurate compass, it is, no doubt, well that he should know the general features of the regular diurnal inequality; but what immediately concerns him is how far the needle is pointing from its mean position at a given hour of a given day. Now, no examination of past data can supply exact prophetic information as to the future, but the present investigation has provided data which will, I trust, enable the practical man to see more exactly how the matter stands, and will give him a more adequate idea of the risks he runs in accepting individual observational data as representative. The statistical data which seem most likely to serve this purpose consist of the mean values of the *absolute daily range* (absolute maximum less absolute minimum) for different months and years, the relative frequency of absolute ranges of specified size, and the frequency with which the absolute maximum and minimum fall at different hours of the day.

§ 19. Table XIV. gives the average value of the absolute daily range for each month of the eleven years as derived from all days disturbed and undisturbed, with the means thence derived for each separate year, and for the twelve months of the average year. The two last rows contain corresponding monthly means derived respectively from all ordinary days and from the Astronomer Royal's quiet days. The two last columns contain yearly means from ordinary days and from quiet days. It is interesting to compare the mean absolute ranges in the second last line of Table XIV. with the mean inequality ranges in the last line of Table VI., these tables both applying to individual months and depending on the observations of exactly the same days. Taking the ratio borne by the absolute to the inequality range, we obtain the following results :—

January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.
2·01	1·89	1·55	1·30	1·29	1·21	1·26	1·24	1·43	1·67	1·90	1·97

The arithmetic mean of these twelve values of the ratio is 1·48. So large an excess in the absolute over the inequality range in ordinary days would hardly, I think, have been anticipated. Relatively considered, the excess of the absolute range is much greater in winter than in summer. The extreme values actually found for the ratio

TABLE XIV.—Absolute Daily Ranges.

Year.	Monthly means from all days.												Yearly means.		
	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	All days.	Ordinary days.	Quiet days.
	′	′	′	′	′	′	′	′	′	′	′	′	′	′	′
1890	8·33	9·25	11·44	11·11	10·49	10·79	10·96	11·55	13·01	13·18	10·79	7·09	10·67	10·49	8·34
1891	7·98	10·92	15·44	16·37	17·03	12·64	13·35	13·86	17·00	16·54	13·54	10·30	13·75	12·84	10·05
1892	12·77	20·75	24·02	17·98	20·33	17·31	20·69	17·99	16·32	17·56	12·93	13·70	17·70	15·36	12·32
1893	13·71	15·19	16·89	17·10	16·01	16·41	16·51	17·55	17·16	15·69	15·14	10·08	15·62	15·17	11·81
1894	12·29	19·50	17·65	17·47	16·61	15·34	18·35	17·72	19·01	16·71	16·56	10·85	16·50	14·67	11·34
1895	12·04	16·59	17·27	17·31	16·65	17·05	15·94	13·57	14·82	17·81	16·96	10·94	15·58	14·80	10·63
1896	16·55	16·96	17·48	16·02	15·67	12·78	13·64	15·04	15·16	13·17	10·70	10·92	14·51	12·92	9·53
1897	9·06	11·24	14·48	16·03	13·15	12·05	12·17	12·69	11·63	11·50	9·66	11·99	12·14	11·48	8·18
1898	9·94	10·14	15·79	12·87	13·07	12·28	12·13	13·27	15·31	13·69	9·69	9·38	12·30	11·19	8·22
1899	9·85	11·99	13·58	12·75	14·40	12·92	11·29	12·02	11·64	10·21	7·62	7·84	11·34	10·54	7·86
1900	10·23	8·07	11·18	10·00	10·54	10·53	10·41	11·15	9·26	8·67	5·23	4·73	9·17	8·86	7·41
Final means from—															
All days . . .	11·16	13·69	15·93	15·00	14·90	13·65	14·13	14·22	14·57	14·07	11·71	9·80	13·57	—	—
Ordinary days .	10·14	11·87	14·19	14·24	13·85	13·26	13·47	13·67	13·71	13·10	10·40	9·00	—	12·57	—
Quiet days . .	6·12	7·57	10·59	11·84	12·09	11·95	11·60	11·93	10·86	9·16	6·54	5·08	—	—	9·61

when individual months were considered were 2·34 in November, 1895, and 1·12 in June, 1900.

Inequality ranges from quiet days are generally less, but only slightly less, than those from ordinary days. Thus, taking the mean diurnal inequalities for the eleven years, the range is 7′·90 for the quiet as against 8′·03 for the ordinary days, the former being thus 98 per cent. of the latter. But the final mean of all the absolute ranges for quiet days in Table XIV., viz., 9′·61, is only 77 per cent. of the corresponding mean for ordinary days. The ratio borne by the quiet day to the ordinary day absolute range is much larger in summer than in winter, varying from 0·90 in June to 0·56 in December. Similarly the ratio borne by the quiet day absolute range to that from all days varies from 0·88 in June to 0·52 in December.

§ 20. The annual variation in the amplitude of the diurnal range presents some interesting features which will be most readily recognised on consulting Table XV.,

TABLE XV.—Monthly Values of Daily Ranges as Percentages of their Arithmetic Mean.

		January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.
Inequality ranges	Quiet days . . .	54	63	110	130	135	131	128	134	120	93	60	43
	Ordinary days .	59	74	107	129	126	128	125	129	113	92	64	54
Absolute ranges	Quiet days . . .	64	79	110	123	126	124	121	124	113	95	68	53
	Ordinary days .	81	94	113	113	110	105	107	109	109	104	83	72
	All days. . . .	82	101	117	111	110	101	104	105	107	104	86	72

where the monthly values are represented as percentages of their arithmetic mean. For comparative purposes data are given for the inequality ranges as well as the absolute ranges.

The two features which the figures are intended to bring out are: (i.) the reduction in the relative importance of the annual variation as we pass from inequality ranges to absolute ranges, and from quiet days to ordinary and to disturbed days; (ii.) the prominence given to a secondary minimum at midsummer and to maxima at the equinoxes in the case of the absolute ranges from ordinary and all days, more especially the latter.

Frequency of Absolute Daily Ranges of Specified Amplitude.

§ 21. Table XIV. shows how the mean value of the absolute range varies from month to month, and from year to year, but this supplies only part of the information wanted. For instance, the mean of the absolute ranges for March was 17 per cent.

TABLE XVI.—Ranges. Number of Occurrences in 11 Years.

Month.		0′ to 5′.	5′ to 10′.	10′ to 15′.	15′ to 20′.	20′ to 25′.	25′ to 30′.	30′ to 35′.	35′ to 40′.	>40′.
January		51	145	69	37	24	7	4	3	1
February		26	99	84	51	26	10	4	2	8
March		1	72	138	61	32	21	8	1	7
April		0	43	167	73	27	10	6	3	1
May		0	57	157	85	20	12	3	0	7
June		0	56	185	67	15	1	3	1	2
July		0	59	185	70	14	5	2	2	4
August		0	37	202	75	22	1	2	0	2
September		1	68	153	71	19	5	4	5	4
October		3	103	111	67	34	10	11	2	0
November		42	140	81	28	14	9	8	5	3
December		64	166	56	29	14	7	1	1	3
Sums	Year	188	1045	1588	714	261	98	56	25	42
	Winter	183	550	290	145	78	33	17	11	15
	Equinox	5	286	569	272	112	46	29	11	12
	Summer	0	209	729	297	71	19	10	3	15

larger than the mean for June. But this may arise in more than one way. It might signify an excess of range in most March days over most June days, or simply that of the comparatively small number of days of very large range a larger proportion occur in the former month than in the latter.

To elucidate this point, the ranges for each month of each year were collected in groups, the first group containing all ranges not exceeding 5′, the second group those exceeding 5′ but not exceeding 10′, and so on. Table XVI. summarises these results for the several months of the year. Totals are also given for the whole period and for the seasons. It seemed simpler to give the actual totals, but any one using the table must remember to divide the figures by 11 if he wishes average results for the months and seasons of a single year. The total number of days included amounted to 4017, of these 1322 occurred in winter, 1342 in equinox, and 1353 in summer. The ranges exceeding 40′ were so few and at the same time so variable that they have been combined to save space. The range exceeded 20′ on 482 days, *i.e.*, on almost exactly 12 per cent. of the days; but in March this percentage rose to 20, whereas in June it fell to 7. One was quite prepared to find that ranges exceeding 20′ are most numerous in the equinoctial months, but their greater frequency at midwinter than at midsummer was quite unexpected.

Table XVII. is based on the same data as Table XVI., but arranges the results under the different years. It also gives means for the average year of the eleven, for the average of the years 1890, 1899, and 1900 of sunspot minimum, and for the average of the years 1892 to 1895 of sunspot maximum.

TABLE XVII.—Ranges. Number of Occurrences in Individual Years.

Year.	0′ to 5′.	5′ to 10′.	10′ to 15′.	15′ to 20′.	20′ to 25′.	25′ to 30′.	30′ to 35′.	35′ to 40′.	>40′.
1890	12	161	155	25	10	1	1	0	0
1891	16	77	157	69	29	5	5	5	2
1892	2	42	132	108	35	16	14	2	15
1893	5	47	124	132	37	11	6	2	1
1894	2	53	159	88	27	13	4	6	13
1895	6	57	136	99	32	18	14	3	0
1896	14	71	157	61	34	15	5	4	5
1897	19	116	155	45	21	5	1	1	2
1898	21	122	149	40	22	6	2	0	2
1899	35	123	147	39	10	6	2	2	1
1900	56	176	117	8	4	2	2	0	0
Yearly averages—									
1890 to 1900	17	95	144	65	24	9	5	2	4
1890, 1899 and 1900	34	153	140	24	8	3	2	1	0·3
1892 to 1895	4	50	138	107	33	14	9	3	7

Ranges of from 10′ to 15′ are about equally numerous in the two classes of years; but ranges over 15′ were $4\frac{1}{2}$ times as numerous in the representative year of sunspot maximum as in the representative year of sunspot minimum, whereas ranges under 10′ were nearly $3\frac{1}{2}$ times as numerous in the representative year of sunspot minimum as in the representative year of sunspot maximum.

Frequency of Occurrence of Maxima and Minima at Different Hours of the Day.

§ 22. Table XVIII. gives the number of occasions during the 11 years when the maximum and minimum for the day fell between 0 and 1 a.m., between 1 and 2 a.m., and so on. The times were measured to the nearest minute. An occurrence at an exact hour, *e.g.* at 2h. 0m., was assigned to the following hour, in the case mentioned 2 to 3. When, as occasionally happened, two hours had equal claims to a maximum or minimum—two measurements agreeing to 0′·1—the occurrence was entered as 0·5 under each hour. Table XVIII. contains results for the three seasons as well as the whole year. Results were really got out for each month, and for the sunspot minimum years 1890, 1899 and 1900, and the sunspot maximum years 1892 and 1895 separately, as well as for the whole 11-year period. The brief abstracts in Tables XIX. and XX. are based on these figures. In these tables the numbers represent percentages, whereas in Table XVIII. they represent the actual number of occurrences. The total occurrences are less in Table XVIII. than in Table XVI., because information was lacking as to the exact hours of maximum or minimum on a few days, more especially in January.

Table XVIII.—Number of Occurrences of Maxima and Minima at Different Hours of the Day.

Hour.	Year.		Winter.		Equinox.		Summer.	
	Maxima.	Minima.	Maxima.	Minima.	Maxima.	Minima.	Maxima.	Minima.
0 to 1	17	338	8	189·5	5	97·5	4	51
1 ,, 2	15	142	7	56	2	48	6	38
2 ,, 3	23	98·5	14	34·5	5	36	4	28
3 ,, 4	18	84	12	23	4	35	2	26
4 ,, 5	15	56	6	16	5	16	4	24
5 ,, 6	19	173·5	8	17	5	18	6	138·5
6 ,, 7	26	376·5	12	5	10	39	4	332·5
7 ,, 8	9	554·5	7	15	2	155	0	384·5
8 ,, 9	9	507	6	77·5	1	286·5	2	143
9 ,, 10	10	100·5	5	45·5	4	45	1	10
10 ,, 11	17·5	2	14	1	3·5	1	0	0
11 ,, noon	159	0	75·5	0	40·5	0	43	0
Noon ,, 1	1293·5	0	476	0	456·5	0	361	0
1 ,, 2	1638·5	0	431·5	0	639	0	568	0
2 ,, 3	518·5	4	121	4	116·5	0	281	0
3 ,, 4	96·5	6	26	5	24·5	1	46	0
4 ,, 5	33·5	33	23	29	2·5	4	8	0
5 ,, 6	28	65	20	25	2	38	6	2
6 ,, 7	20	125	18	55	2	60	0	10
7 ,, 8	4	211·5	2	107·5	1	84	1	20
8 ,, 9	5	273	2	138·5	2	105·5	1	29
9 ,, 10	5	283	3	164	1	95	1	24
10 ,, 11	4	271·5	0	154	2	78	2	39·5
11 ,, midt.	7	303·5	4	159	2	95·5	1	49
Totals . .	3991	4008	1301	1321	1338	1338	1352	1349

§ 23. Considering the large excess of the average absolute range over the average inequality range, it is surprising to find that such a very large proportion of the maxima occur within $1\frac{1}{2}$ hours of the time of the maximum in the inequality range for the year. It is no less surprising to find that on no single day of the whole 4008, for which information existed, did the minimum fall between 11 a.m. and 2 p.m. In the case of the minima the frequency of occurrence shows an unmistakable double period at all seasons; the maxima of frequency fall at about midnight, and between 7 and 9 a.m., the former being the more important in winter, but the latter at the other seasons. There is probably also a double period in the frequency of occurrence of the maxima, but the secondary maximum of frequency is very small, and a longer period of years would be required to show the exact hour of its occurrence at the different seasons.

TABLE XIX.—Incidence of Maxima. Percentages of Totals.

	Year.			Winter.			Equinox.			Summer.		
	Sunspot minimum.	11 years.	Sunspot maximum.	Sunspot minimum.	11 years.	Sunspot maximum.	Sunspot minimum.	11 years.	Sunspot maximum.	Sunspot minimum.	11 years.	Sunspot maximum.
Midt. to 10 a.m.	3·6	4·1	4·6	7·1	6·5	6·0	1·6	3·2	4·9	2·2	2·4	2·9
10 a.m. ,, 11 a.m.	0·3 } 94·9	0·4 } 93·3	0·3 } 91·9	0·8 } 89·2	1·1 } 88·0	0·6 } 87·2	0·0 } 98·1	0·3 } 95·7	0·2 } 93·3	0·0 } 97·3	0·0 } 96·1	0·0 } 95·1
11 a.m. ,, noon	4·5	4·0	3·0	6·9	5·8	4·2	3·3	3·0	2·3	3·5	3·2	2·6
Noon ,, 1 p.m.	40·2	32·4	27·4	46·9	36·6	28·6	40·5	34·1	30·4	33·3	26·7	23·4
1 p.m. ,, 2 p.m.	38·7	41·1	43·9	29·2	33·2	37·7	47·7	47·8	48·7	39·0	42·0	45·0
2 p.m. ,, 3 p.m.	10·1	13·0	14·4	4·8	9·3	12·7	5·2	8·7	9·5	20·1	20·8	21·0
3 p.m. ,, 4 p.m.	1·1	2·4	2·9	0·6	2·0	3·4	1·4	1·8	2·2	1·4	3·4	3·1
4 p.m. ,, midt.	1·5	2·6	3·5	3·7	5·5	6·8	0·3	1·1	1·8	0·5	1·5	2·0

TABLE XX.—Incidence of Minima. Percentages of Totals.

	Year.			Winter.			Equinox.			Summer.		
	Sunspot minimum.	11 years.	Sunspot maximum.	Sunspot minimum.	11 years.	Sunspot maximum.	Sunspot minimum.	11 years.	Sunspot maximum.	Sunspot minimum.	11 years.	Sunspot maximum.
Midt. to 10 a.m.	62·5	60·6	62·2	33·7	36·2	40·0	64·6	58·1	57·9	88·6	87·1	88·5
10 a.m. ,, 4 p.m.	0·3	0·3	0·4	0·6	0·8	0·8	0·3	0·2	0·2	0·0	0·0	0·0
4 p.m. ,, midt.	37·2	39·1	37·4	65·7	63·0	59·2	35·1	41·7	41·9	11·4	12·9	11·5

Table XIX. is principally intended to bring out two facts: (1) that the hour of most frequent occurrence of the daily maximum is earlier in years of sunspot minimum than in years of maximum; (2) that the distribution of maxima is more concentrated, *i.e.* less uniform throughout the 24 hours, in years of sunspot minimum than in years of maximum. The phenomenon first mentioned is most conspicuous in winter. As regards the second phenomenon, there is an apparent exception in winter, the occurrences between midnight and 10 a.m. then diminishing slightly with increased sunspot frequency. This diminution is, however, more than made up for by the increase in the occurrences between 4 p.m. and midnight, and it probably merely represents the tendency to a closer approach to equality between the morning and evening occurrences which is seen in sunspot maximum years at the other seasons.

In the case of the daily minima, the differences between the phenomena in years of sunspot maximum and minimum are small. Table XX. does, however, show that in winter and equinox there is, in the years of sunspot maximum, a reduction in the disproportion of the evening and morning occurrences.

Annual Variation. Fourier Coefficients.

§ 24. The mean monthly values of an element during the year may be analysed in a Fourier series

$$M + P_1 \sin (t + \theta_1) + P_2 \sin (2t + \theta_2) + \ldots,$$

where t denotes time counted from January 1st, 30° being taken as the equivalent of one month. M denotes the arithmetic mean of the 12 monthly values, P_1 and P_2 the amplitudes of the annual and 6-month terms, while θ_1 and θ_2 represent the phase angles. One month of time answers, of course, to 30° in θ_1, to 60° in θ_2, and so on.

In determining the constants the observed monthly values were treated as if separated by exactly equal intervals of time. This is not strictly true, and there is a corresponding slight uncertainty in the results. Practically the same uncertainty enters, however, into the several groups of years and the different species of days, and the principal object of the investigation was to detect *differences* between the phenomena of the different groups of years or of the different classes of days.

Table XXI. shows the results obtained, including for comparison some already published for quiet days. In the case of the diurnal inequality, the first place has been given to the sum of the 24 differences from the mean for the day. This element is much less dependent on the accident of local time than is the range, and is probably a more accurate measure of the activity of the forces to which the diurnal inequality is due.

Contrasting ordinary and quiet days, we see that whilst M is invariably greater for the former, this is not the case with P_1. Thus P_1/M—or the fraction of the

TABLE XXI.—Annual Variation. Fourier Coefficients.

Element.	Nature of days.	Period.	M.	P_1.	P_2.	θ_1.	θ_2.	P_1/M.	P_2/M.	P_2/P_1.
			′	′	′	°	°			
Sum of 24 hourly differences .	Ordinary	1892 to 1895	59·17	19·54	6·69	282	283	0·330	0·113	0·34
,, ,, ,, .	,,	11 years	49·19	17·60	5·83	278	285	0·358	0·118	0·33
,, ,, ,, .	,,	1890, 1899, 1900	39·15	15·96	4·33	273	289	0·408	0·110	0·27
,, ,, ,, .	Quiet	1892 to 1895	50·60	19·80	4·47	278	297	0·391	0·088	0·23
,, ,, ,, .	,,	11 years	41·68	17·54	4·97	274	291	0·421	0·119	0·28
,, ,, ,, .	,,	1890, 1899, 1900	33·75	16·52	3·39	275	282	0·490	0·101	0·21
Inequality range	Ordinary	11 years	8·44	3·36	0·94	279	280	0·398	0·111	0·28
,, ...	Quiet	,,	8·03	3·81	1·22	275	273	0·474	0·152	0·32
c_1	Disturbed	,,	5·27	1·05	0·76	319	228	0·199	0·144	0·72
c_1	Ordinary	1892 to 1895	3·53	1·20	0·29	280	296	0·339	0·083	0·25
c_1	,,	11 years	2·91	1·05	0·25	276	300	0·361	0·086	0·24
c_1	,,	1890, 1899, 1900	2·29	0·94	0·18	272	311	0·411	0·080	0·20
c_1	Quiet	1892 to 1895	2·91	1·23	0·18	277	318	0·422	0·063	0·15
c_1	,,	11 years	2·37	1·09	0·17	274	304	0·459	0·073	0·16
c_1	,,	1890, 1899, 1900	1·86	0·97	0·12	274	303	0·519	0·063	0·12
Absolute range	All	11 years	13·57	1·67	1·64	295	287	0·123	0·121	0·98
,, ...	Ordinary	,,	12·57	2·15	1·40	281	285	0·171	0·112	0·65
,, ...	Quiet	,,	9·61	3·34	1·14	280	282	0·347	0·118	0·34

element which takes part in the annual variation—is in all cases less for the ordinary than for the quiet days. P_2, on the contrary, distinctly increases as we pass from quiet to ordinary days, and sometimes in a larger proportion than M. The importance of the 6-month term as compared to the 12-month term is thus, in general, notably greater for the ordinary than the quiet days. It seems specially great for the disturbed days.

P_1 and P_2 both rise with increase in sunspot frequency, but P_1 increases less relatively than M, and P_1/M falls notably.

We thus see that, relative to the mean value of the element, the term whose period is 12 months is most conspicuous on quiet days and when sunspots are few.

Coming to the phase, as I have pointed out before, θ_1 and θ_2 for quiet days both increase with sunspot frequency, *i.e.* the times of occurrence of the maxima are earlier for both the 12-month and 6-month terms in years of sunspot maximum than in years of sunspot minimum. The value of θ_1 for ordinary days exhibits the same phenomenon, but to an enhanced degree. Taking the 24 differences, the inequality range, and c_1, the mean difference in time was only 3·4 days in the case of the quiet days, whereas for the ordinary days the mean difference in time from the 24 differences and c_1 is 8·9 days. Ordinary days show, however, a diminution in θ_2, or a retardation of phase in the 6-month term, as we pass from sunspot minimum to sunspot maximum.

Comparing ordinary and quiet day phases, we find that θ_1 is greater for the former, except in years of sunspot minimum. Taking a mean from the 11-year data for the 24 differences, the inequality range, and c_1, the maximum in the 12-month term occurs 3·1 days earlier for the ordinary than the quiet days. The advance of phase is still more notable in the cases of c_1 from disturbed days, and of the absolute range from all days. The results for the influence of disturbance on θ_2 appear somewhat contradictory.

Sunspot Relationships.

§ 25. In the previous part of the paper there have been a number of references to sunspot frequency, but all with the object of illustrating the differences that exist between the phenomena of different years. The remainder of the paper is exclusively devoted to a study of the sunspot relationship, but from a somewhat different point of view.

In A, I investigated whether the average sunspot frequency after WOLFER was less for the Astronomer Royal's quiet days than for days as a whole. The quiet days are practically free from magnetic disturbance, thus, if disturbance is intimately connected with the *simultaneous* sunspot frequency, one would expect the mean sunspot frequency from the quiet days of a month to be notably less than that from the month as a whole. The comparison was made for the 11 years 1890 to 1900 (A, pp. 433, 434), and showed that if any real difference existed between sunspot frequency for quiet days and for other days, it must be exceedingly small. Assuming WOLFER's frequencies an appropriate measure of the phenomenon, this seemed practically conclusive against any theory which postulates a direct relationship without time lag between sunspot frequency and magnetic disturbance.

It is clear, however, as I fully recognised at the time, that the result does not necessarily militate against any theory which supposes a day or more to elapse between the phenomenon on the sun and the corresponding phenomenon on the earth. Since the paper was written, ARRHENIUS and others have advanced theories —and evidence regarded as favourable to the theories—which postulate the transfer from the sun of electrified matter or ions at a rate very slow compared to that of light. ARRHENIUS considers two days as about the time required to reach the earth. Again, there are a considerable number of days for which WOLFER has no sunspot data, and in some months this was the case for more than one of the Astronomer Royal's quiet days. I accordingly decided to repeat the investigation, at the same time widely extending its scope and replacing WOLFER'S frequencies by the Greenwich daily values of sunspot areas. These, being based on data from India and Mauritius, as well as Greenwich, are seldom lacking for more than 2 or 3 days in the year.

Sunspot areas, as given at Greenwich, are of two kinds, *projected* areas and *corrected* areas. The former are the areas as seen and measured in photographs, expressed as millionths of the sun's apparent disc; the latter are corrected for foreshortening. I have made use of the projected areas, principally because these are collected and presented in a convenient table in the annual Greenwich volumes. The corrected areas are of course the more correct measure of the state of spottedness of the visible hemisphere, but if the action exerted by the sun is a species of bombardment, as seems postulated by the views of ARRHENIUS, MAUNDER, and others, the projected area should be the more appropriate for the present purpose.

§ 26. The first results I shall discuss relate to the quiet and disturbed days. The days of each month were arranged in three approximately equal groups, according to sunspot areas. Normally the first and third groups contained respectively the 10 days of largest and the 10 days of least sunspot area, the second group containing the intermediate days. It was then investigated into which groups the quiet and the disturbed days fell.* This was done for each month of the 11 years. If the sole cause of magnetic disturbance lay in simultaneous solar action dependent on sunspots, what we would expect to find would be all the disturbances falling under Group I. days, and all quiet days under Group III.

In carrying the scheme into execution a difficulty was encountered, viz., that in 1890, 1899, and 1900 there were months—21 in all—in which more than 10 days were wholly free from spots. It being impossible to get equal groups in these

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* The more natural process would have been to compare the mean sunspot areas for the quiet and the disturbed days with the mean area for the month; but this would have entailed the calculation of the monthly means, which do not seem to be given in the Greenwich volumes.

months, they are omitted in Table XXII. which summarises the results of the investigation.

The conclusions drawn from Table XXII. will, I suspect, depend a little on the temperament of the reasoner. There is a deficit of quiet days and an excess of disturbed days in the group of days of largest sunspot area, the excess of disturbed days being the more conspicuous. But whilst the mean from the whole 11 years appears favourable to a *slight* connection between disturbance and simultaneous sunspot area, there are individual years (*e.g.* 1895 and 1899) which associate quiet days with large sunspot area, and some (1895, 1897, and 1899) which associate disturbances with small sunspot area.

TABLE XXII.—Occurrences of Quiet and of Disturbed Days.

	Quiet days. (Number found in each group.)			Disturbed days. (Number found in each group.)		
Groups . . .	I.	II.	III.	I.	II.	III.
1890	5	6	4	0	0	0
1891	19	18	23	4	11	6
1892	17	23	20	8	16	6
1893	20	16	24	6	2	3
1894	20	18	22	10	7	4
1895	21	21	18	4	6	9
1896	22	18	20	15	11	11
1897	18	22	20	5	2	7
1898	16	23	21	8	7	4
1899	14	21	10	6	3	8
1900	7	9	9	2	0	0
Totals . . .	179	195	191	68	65	58
Percentages .	31·7	34·5	33·8	35·6	34·0	30·4

The mean sunspot areas for the whole 11 years were, in the Greenwich units, 1626 from the group of largest areas, as against 312 from the group of least area. Thus the difference between the days of Groups I. and III. as regards sunspot area was very large. Taking this into account, we must, I think, conclude that the results of Table XXII. are incompatible with any theory which regards magnetic disturbance as dependent directly *in any large degree* on the *simultaneous* extent of the projected sunspot area. Further, even if we assume that no appreciable accidental element enters into the mean results of Table XXII., and that they would be reproduced in means derived from a whole century, it would not *necessarily* prove the slightest connection of the kind mentioned.

Sunspot area, it is true, shows a far from regular progression from day to day; the area on one day is not infrequently a considerable multiple of that on the preceding day. But, as a rule, days of large area and days of small area occur in groups. In one or two months the 10 days of largest area were absolutely consecutive, and it was rather the rule than the exception for a considerable proportion of the days of both Groups I. and III. to be consecutive. Thus the phenomena of Table XXII. might be expected to occur though there were no direct connection between disturbance and the simultaneous solar phenomena, provided there were an effect on the earth within a few days of the occurrence on the sun. The results, in short, might be easily reconciled with theories such as that of ARRHENIUS.

§ 27. The next and much more laborious investigation was intended to throw light on ARRHENIUS' and similar theories. If there is an influence originating in the sun, whose intensity increases synchronously with sunspot area, which is propagated to the earth in two or three days and there causes magnetic storms, then there ought to be a marked association between the amplitude of the absolute daily range and the sunspot area two or three days previously. To investigate this point the 10 days of largest and the 10 days of least absolute range in each month were taken to form two contrasted groups. The sunspot areas answering to each of these days and the three preceding days were entered in four successive columns, and means were formed for each month. One thus got for each month four mean sunspot areas S, S_{-1}, S_{-2}, S_{-3}, answering: S to the 10 days of largest absolute range, S_{-1} to the 10 days immediately preceding these, and so on, and four mean areas S′, S'_{-1}, S'_{-2}, S'_{-3}, answering to the 10 days of least absolute range, to the 10 days preceding these, and so on.

What appears in Table XXIII. is the algebraic excess of the 12 monthly values of S, S′ . . . over the mean sunspot area for the year as given by the Astronomer Royal. The second last line gives the algebraic mean of the above results from the 11 years. The last line gives the final mean obtained when the entries under each individual year are expressed as percentages of the mean sunspot area for that year. In the headings of the columns, n is intended to denote the representative day of large (or small) absolute range; $n-1$, $n-2$, and $n-3$ the three preceding days in order.

If magnetic disturbance were entirely or even largely due to solar influence, whose activity at its source was largely dependent on sunspot area, and whose time of propagation to the earth varied only within narrow limits, then what one would expect to see would be a notable excess in the mean S_{-1}, S_{-2}, or S_{-3}, and a corresponding deficit in the mean S'_{-1}, S'_{-2}, or S'_{-3}.

If the principal source of magnetic disturbance is of the kind postulated, but the time of propagation to the earth varies largely from under a day to several days, then what one would expect is an excess of all or most of the S's, with corresponding deficits in S″s.

It is the second hypothesis, if either, which derives support from Table XXIII. In

TABLE XXIII.—Algebraic Excess of Sunspot Areas over the Mean for the Year.

Year.	Days of largest range.				Days of least range.			
	n.	*n* − 1.	*n* − 2.	*n* − 3.	*n*.	*n* − 1.	*n* − 2.	*n* − 3.
1890	− 26	− 23	− 17	− 5	+ 8	0	− 6	− 12
1891	− 13	− 24	− 19	− 12	+ 31	+ 82	+ 53	+ 22
1892	+ 38	+108	+155	+226	−125	−141	−203	−201
1893	+ 4	+ 33	+ 72	+100	+ 6	− 20	− 62	−122
1894	+170	+147	+127	+108	−177	−187	−179	−165
1895	+ 14	+ 2	− 47	− 92	+ 6	+ 20	+ 40	+ 85
1896	+ 28	+ 37	+ 35	+ 48	− 72	− 71	− 51	− 6
1897	+ 23	+ 7	+ 24	+ 48	+ 37	+ 15	− 10	− 36
1898	+118	+106	+ 93	+ 66	−143	−130	−114	− 85
1899	+ 5	+ 8	+ 13	+ 19	+ 31	+ 27	+ 14	+ 6
1900	+ 24	+ 27	+ 20	+ 26	− 7	− 8	− 15	− 23
Means . . .	+ 35	+ 39	+ 41	+ 48	− 37	− 38	− 48	− 49
Percentages .	+4·4	+5·1	+4·9	+6·8	−2·5	−2·9	−5·1	−6·4

some individual years, *e.g.* 1892, 1893, 1894, 1898, and 1900, the phenomena are so far distinctly favourable to views such as ARRHENIUS', if we suppose the velocity of propagation from the sun highly variable. But even in these years the balance in excess of the S's, and of deficit in the S′'s, appears very small when we consider the great disproportion which exists between the means of the ten largest and the ten least absolute ranges.

A remarkable feature in Table XXIII. is the comparative regularity in the values of the successive S's and S′'s in any one year. But whether the trend of the sequence is to a rise or a fall seems largely fortuitous. Thus we have a regular rise from S to S_{-3} in 1892, but a regular fall in 1894. The phenomenon is probably due in part to the tendency for days of largest and of least sunspot area to occur in groups.

Whilst the mean results in Table XXIII. suggest a closer connection of the range with the sunspot area two or three days previously than with that of the day itself, still we have a difference of 6·9 between the final percentage values in the first and fifth columns of Table XXIII. as against a corresponding difference of 13·2 between the fourth and eighth columns. Any theory which requires as much as one day for the minimum time of transfer of disturbance from the sun to the earth has thus the evidence in its favour very considerably weakened. In every year, it should be mentioned, individual months gave results diametrically opposed to the final mean.

§ 28. The excess of S over S′, and the pre-eminence of S_{-3} in the final means, pointed to the desirability of further enquiry. The scheme of operations leading up to Table XXIII. was accordingly repeated, but with this difference, that the comparison instituted was between the *five* days of largest and the five of least range in the month, and it was extended to include the fourth previous day and the day following that to which the range belonged.

The increase in the difference between the mean ranges in the two groups of days due to the reduction of the number of days in the group from 10 to 5 is shown in Table XXIV. The final means from the 11 years for the groups of largest and of least range bear the ratio of 2·18 when the monthly groups contain 10 days, but 2·92 when they contain 5 days. Thus what we should expect in Table XXV., which summarises the investigation for 5-day groups, is a repetition of the phenomena apparent in Table XXIII., but in a considerably enhanced degree. The tables were prepared exactly in the same way and the headings have the same meanings; $n+1$ denotes of course the day following that to which the magnetic range belongs. The column under the first heading, $n+1$, is spoken of as the first column.

TABLE XXIV.—Mean Absolute Ranges.

Year.	Groups of 10.		Groups of 5.	
	Largest.	Least.	Largest.	Least.
	′	′	′	′
1890	14·37	7·57	16·32	6·88
1891	19·80	9·03	23·59	8·24
1892	26·88	11·03	34·74	9·97
1893	21·03	11·28	24·27	10·29
1894	24·89	10·77	31·79	9·84
1895	22·32	10·26	25·72	9·29
1896	21·76	9·28	26·13	8·40
1897	17·71	7·93	21·35	7·00
1898	18·51	7·78	22·99	7·02
1899	16·41	7·49	19·90	6·77
1900	12·41	6·42	14·58	5·94
Means	19·64	8·99	23·76	8·15

It will be seen that the final excesses in the means for columns 2 to 5 over those for columns 8 to 11 is greater in Table XXV. than in the corresponding columns of Table XXIII. This result is favourable to the view that the difference is not purely fortuitous, but betokens some physical connection.

The marked rise in the mean of the second column, as compared to that of the first column in Table XXV., is also distinctly favourable to this view. On the other hand, the mean for the seventh column is nearly as large numerically as those for columns 8 to 10, and larger than the means for columns 11 and 12. This is equivalent to the effect occurring 24 hours in advance of the cause. An explanation may, to some extent, be forthcoming from the fact that there is a tendency for days of large range and of small range to occur in groups. This tendency is, however, markedly less than the corresponding tendency in the case of sunspot areas already alluded to (a difference of significance in itself), and it is unusual to have more than two or three successive days on which the ranges are all markedly greater or markedly less than the mean for the month.

TABLE XXV.—Algebraic Excess of Sunspot Areas over the Mean for the Year.

Year.	Days of largest range.						Days of least range.					
	$n+1$.	n.	$n-1$.	$n-2$.	$n-3$.	$n-4$.	$n+1$.	n.	$n-1$.	$n-2$.	$n-3$.	$n-4$.
1890	− 46	− 35	− 41	− 41	− 28	− 11	+ 28	+ 31	+ 18	+ 1	− 13	− 28
1891	− 44	− 59	− 84	− 56	− 32	+ 1	− 24	− 26	− 46	− 64	− 69	− 98
1892	−105	+ 32	+161	+223	+321	+408	− 53	−186	−205	−230	− 98	−142
1893	− 49	+ 90	+196	+240	+245	+207	+140	+163	+186	+162	+160	+ 83
1894	+106	+184	+201	+182	+154	+212	−320	−366	−364	−334	−296	−251
1895	−130	−152	−161	−194	−229	−216	− 53	− 27	− 29	+ 8	+130	+220
1896	+ 57	+ 72	+ 69	+ 83	+ 67	+ 30	−128	−123	−112	−127	−108	−114
1897	− 20	+ 28	+ 15	+ 33	+ 76	+135	+ 78	+ 78	+ 80	+ 46	+ 30	− 42
1898	+207	+171	+180	+158	+110	+ 70	−246	−258	−208	−166	−130	− 64
1899	+ 46	+ 50	+ 53	+ 51	+ 56	+ 41	+ 11	+ 24	+ 47	+ 48	+ 42	+ 34
1900	+ 27	+ 54	+ 57	+ 55	+ 57	+ 66	− 8	− 9	− 13	− 4	− 3	+ 15
Means . .	+ 4	+ 40	+ 59	+ 67	+ 72	+ 86	− 52	− 64	− 59	− 60	− 32	− 35

§ 29. A minute comparison of Tables XXV. and XXIII. brings out some very curious features, which seem explicable only in the view that accident plays a large part in the mean results for any single year. In 1890, 1891, and 1895, the entries under n, $n-1$, $n-2$, and $n-3$ for the days of largest range are not merely negative in Table XXV., but are conspicuously more so than the corresponding entries in Table XXIII. In 1893 the entries under $n-1$, $n-2$, and $n-3$ for the days of least range in Table XXIII. were negative, but in Table XXV. the corresponding entries are positive and large. Thus in this year the phenomena for the five days of largest and the five of least range a month differ notably from the phenomena for the average day, but they differ in the same direction. With the exception of 1894, 1898 is the year in which the sunspot phenomena from the two groups of days differ most; but this difference is largest for the columns headed $n+1$, *i.e.* for the days *subsequent* to those of largest range.

§ 30. Considering the contradictions in Table XXV., it appeared desirable to obtain corresponding results for the different months of the year from the 11 years combined. They appear in Table XXVI. The headings have the same meaning as before. As,

TABLE XXVI.—Magnetic Ranges and Sunspot Areas in Contrasted Groups of Five Days.

Month.	Five days of largest range.							Five days of least range.						
	Range.	Mean sunspot areas.						Range.	Mean sunspot areas.					
		$n+1$.	n.	$n-1$.	$n-2$.	$n-3$.	$n-4$.		$n+1$.	n.	$n-1$.	$n-2$.	$n-3$.	$n-4$.
	′							′						
January	22·90	795	807	776	716	691	758	5·07	980	1001	986	940	1006	943
February	27·21	1094	1168	1198	1239	1296	1323	6·55	1042	997	1065	1006	1055	886
March	29·87	809	842	852	851	869	878	8·93	647	590	564	563	567	605
April.	23·69	733	802	874	891	893	822	10·31	838	822	810	807	794	757
May	25·36	760	774	747	753	782	786	9·50	706	741	763	798	852	914
June.	19·92	973	1030	1101	1116	1117	1063	9·89	771	750	754	778	848	913
July	22·49	918	982	1134	1299	1394	1467	9·96	805	802	806	823	838	889
August	21·27	1232	1297	1287	1189	1124	1103	10·05	1040	978	945	929	935	948
September	24·55	1133	1180	1190	1211	1212	1242	9·52	772	733	752	804	848	914
October.	23·92	624	631	665	670	679	717	8·01	927	981	993	969	963	979
November	23·58	706	675	615	541	505	547	5·64	638	642	674	693	681	615
December	20·43	911	918	916	956	939	955	4·36	839	834	816	804	859	851
Means . . .	23·77	891	926	946	953	958	972	8·15	834	823	827	826	854	851

however, the mean sunspot areas from all days were not known for individual months, absolute sunspot areas are given in the several columns. The corresponding magnetic ranges are shown.

Table XXVI. shows that contradictions exist between different months, just as between different years. In several months the left-hand side of the table (*i.e.* the half dealing with the days of largest range) supports the view that magnetic disturbance is even largely dependent on the sunspot area three or four days previously. February and July are outstanding examples, the increase in sunspot area from day $n+1$ to day $n-4$ being most marked. Again, in the majority of months—*e.g.* February, March, June, July, August, September and December—the areas in the several columns of the left-hand side exceed those in any of the columns of the right-hand side. But diametrically opposite phenomena appear in more than one month. In May and November, taking corresponding columns from the two halves of the table, the sunspot area on the right-hand side is the larger from day $n-1$ to day $n-4$. In January and October the smallest sunspot area on the right-hand side is larger—and notably larger—than the largest area on the left-hand side. A seasonal change in the amplitude of a phenomenon causes no surprise, but a seasonal change which absolutely alters the sign of a phenomenon, so that January is opposed to December, and October to September, is, I think, without precedent.

As regards the right-hand side of Table XXVI., we know already, through Table XXV., that the means from the months combined are all below the mean sunspot area for the 11 years. This is almost the only feature favourable to an association of sunspots and magnetic ranges of the kind suggested by the mean values on the left-hand side. In April, indeed, the sunspot area shows a progressive though small decline from day $n+1$ to day $n-4$, but May shows the opposite phenomenon, and so do June, July, and September, from day n to day $n-4$.

§ 31. An independent investigation was made on the lines of § 27, taking the ten days of largest and the ten days of least sunspot area in each month as the contrasted groups, and comparing the absolute magnetic ranges on these days and the three *following* days. The results obtained were generally similar to those in § 27, but the apparent association of sunspot frequency and magnetic range in the final means from the 11 years was only about half that shown by Table XXIII.

An investigation was also made on the lines of § 27, but employing Greenwich projected areas of faculæ for those of sunspots. This was limited to a single year, 1892, the results obtained being at least as contradictory and as unfavourable to any *intimate* relationship of cause and effect as the corresponding results from sunspot area.

Discussion of Remarkable Special Cases.

§ 32. During the investigation into sunspot areas, some individual instances were noticed of a highly suggestive character. In August, 1890, the largest range occurred in a day which with its three preceding days showed no sunspot. In October, 1890, the largest spotted area encountered on the five days of largest range, or during the 4-day periods preceding them was only 120, whereas the mean of the sunspot areas for the four days of smallest range and the 4-day periods preceding them were as follows:—

Day	n.	$n-1$.	$n-2$.	$n-3$.	$n-4$.
Sunspot area	1095	1089	970	714	597

In this instance the ranges in the two cases were widely different, the means being 22′·9 for the five days of largest range, and only 6′·7 for the four days of least range.

February 1, 1893, was a "quiet" day, and had a range 3′ less than that on any other day of the month. It had, however, the largest spot area of the month, and the four immediately preceding days in January had all spot areas larger than that of any single day in February.

In April, 1894, the two days of largest range were the days of least spot area for the month, and the four preceding days in each case were included in the group of ten days of least spot area.

In November, 1895, not one of the nine days of largest range came into the group of ten days of largest spot area, and the day of the absolutely largest range was the day of absolutely least spot area.

In February, 1896, the two days of largest spot area were both "quiet" days, and had the smallest ranges of any in the month.

In October, 1896, not one of the nine days of largest range—four of them disturbed—nor of the four days preceding them came into the group of ten days of largest spot area.

In October, 1897, the day of largest range but one—itself a disturbed day—and the four previous days were all free from spots, though only three other days in the month were similarly situated.

During February, 1899, there were three "disturbed" days—one showing a range of 45′—and all three were free from any sunspot, though sunspots occurred on 17 days of the month.

In 1900 the sunspot area was absolutely nil from November 24 to December 31. December is the month of minimum range, and so the amplitude of the regular diurnal variation naturally would vary but little throughout the month. Thus if an intimate connection of any kind—possessing a time lag of any length up to six days—really existed between range and sunspot area, what we would have expected to find would have been a nearly constant daily range. What actually did happen is shown by the following figures:—

Mean of absolute ranges on the ten days of—		Mean of absolute ranges on the five days of—	
Largest range.	Least range.	Largest range.	Least range.
′ 7·3	′ 3·0	′ 9·4	′ 2·7

The two days having the absolutely largest ranges were the 27th and 28th, and so were preceded by over 30 days free from spots.

The above instances are probably amongst the most striking examples of their kind, but many others scarcely less striking could be adduced. No doubt a similar number of striking associations of large ranges and large sunspot areas exists, but if the one set of phenomena must be ascribed to chance, may not also the other ?

The phenomena of December, 1900, alone suffice to demonstrate that considerable variations are possible in the range without the occurrence for a month previously of any sunspot of measurable area. Thus, unless a time lag exceeding a month is postulated, we seem obliged to conclude that there are agencies other than those associated with visible sunspots which exert a potent influence on the range of the magnetic needle. The immediate source may, of course, be the sun, if the visible sunspot is only an accidental concomitant of the electrical disturbance and not an essential phenomenon. But it seems equally possible that the disturbances at the sun, visible as sunspots, and the enlargement of the magnetic range, are due to a common cause, operating throughout the solar system, but with an intensity which at any given instant may vary widely at points as far apart as the earth and sun.

One possibility which may be mentioned, if only to show that it was not overlooked, is that the ions, electrons, emanations—or whatever is the appropriate term for the entity supposed to be propagated from the sun—may have properties which show only a gradual decay when in the earth's atmosphere. Thus the condition on any given day, in that part of space—if external to the earth's surface—whence originate the causes of magnetic movements, regular and irregular, may be represented by an integral which receives contributions from a number of previous days. This is at least consistent with the continuous large amplitude of the diurnal inequality which is characteristic of years of many sunspots.

It must be remembered, however, that disturbances seldom continue large for more than two or three days, often less, and that quiet days often follow hard on them ; on the other hand, magnetic storms often reach a great intensity within a few hours after a prolonged quiet or but slightly disturbed time. The immediate cause of at least some forms of magnetic disturbance must thus be something which is capable of very rapid changes, and whose effects may die out, if not instantaneously, at least very rapidly.

Applications of WOLF's *Formula.*

§ 33. If any element, R, varies in a linear way with sunspot frequency, its value must be expressible by a formula of the type

$$R = a+bS,$$

where S denotes sunspot frequency, while a and b are constants. This formula, originally due to WOLF, has been applied to the range and the sum of the 24 differences in the diurnal inequality derived from individual months of the year. The inequalities employed in the calculation were not those from individual years, but those from the sunspot maximum years 1892 to 1895 combined, the sunspot minimum years 1890, 1899, and 1900 combined, and the whole 11 years combined. The method followed was that explained in A, p. 418. The results appear in Table XXVII.

TABLE XXVII.—Diurnal Inequality from all Ordinary Days.

	Range.			Sum of 24 differences.		
	a.	$b \times 10^4$.	$(b/a) \times 10^4$.	a.	$b \times 10^3$.	$(b/a) \times 10^4$.
January	3·97	238	60	21·26	207	98
February	4·26	422	99	24·04	357	149
March	6·72	665	99	35·03	523	149
April	8·69	542	62	45·36	352	78
May	8·46	509	60	45·97	328	71
June	8·84	458	52	48·96	305	62
July	8·18	537	66	45·65	338	74
August	9·40	354	38	52·44	190	36
September . . .	7·39	466	63	40·83	355	87
October	6·11	388	64	34·22	341	100
November . . .	4·28	312	73	23·16	272	118
December . . .	3·44	254	74	17·95	201	112
Year	6·65	428	67	36·24	314	94
Winter	3·99	304	76	21·60	259	119
Equinox	7·23	515	72	38·86	393	103
Summer	8·72	465	54	48·25	290	61

The values assigned to the year and the seasons are arithmetic means from the months included. The results correspond exactly to those given in A, Table XLI., for quiet days.

Absolutely considered, b is least in winter, but relatively to a it is then greatest. In this respect the phenomena are similar to those observed on quiet days, but b/a is less variable with the season on ordinary than on quiet days.

It will be noticed that b/a is larger for the sum of the differences than for the range; the same phenomenon appeared in the case of the quiet days, but less conspicuously.

§ 34. The formula was also applied to the means of the 12 monthly values for individual years of the inequality range from ordinary days, and to the absolute ranges from quiet days, ordinary days, and all days. The method of least squares was employed.

Table XXVIII. gives the results found. It also gives $\bar{D}$, the arithmetical mean of the differences between the observed and calculated yearly values, and E, the corresponding probable error. The mean difference and the probable error are also expressed as percentages, the former of the mean value of the element, the latter of the range of the element (or difference between the greatest and least of the yearly values).

TABLE XXVIII.—Values of Constants in WOLF'S Formula, and Resulting Accuracy.

		a.	$b \times 10^4$.	$(b/a) \times 10^4$.	Mean differences calculated and observed. $\bar{D}$.	Probable error. E.	$\frac{\bar{D} \times 100}{\text{Mean value}}$.	$\frac{\text{E} \times 100}{\text{Range}}$.
					′	′		
Inequality range, all ordinary days		6·68	441	66	0·18	0·15	2·2	4·0
Absolute range,	quiet days .	7·23	571	79	0·44	0·37	4·6	7·5
	all ordinary days	9·48	741	78	0·51	0·43	4·0	6·6
	all days . .	9·95	867	87	0·65	0·64	4·8	7·5

In the case of the inequality range, the agreement between the observed values and those calculated from WOLF'S formula is remarkably close. In five out of the eleven years the difference between the observed and the calculated value was less than 0′·1, and the largest difference was only 0′·33. This is noteworthy, considering that the element varied from 6′·83 to 10′·74. In the case of the absolute ranges the agreement is very decidedly less good, but, absolutely considered, it is still very fair, especially for the ordinary days.

The cost of measuring and tabulating the curves was defrayed in large measure by a grant obtained in 1904 from the Government Grant Committee. The arithmetic necessary for the construction of the tables was very heavy, and I have had valuable assistance in this direction from several members of the staff of the National Physical Laboratory, especially Mr. B. FRANCIS and Mr. G. BADDERLY. In smoothing the curves and in other directions I had much assistance from Mr. T. W. BAKER, the Chief Assistant of the Observatory Department, who had charge of the magnetic instruments during the whole period dealt with. Every care has been taken to secure accuracy in the calculations.

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THE EFFECT OF HYDROGEN ON THE DISCHARGE OF NEGATIVE ELECTRICITY FROM HOT PLATINUM

BY

PROFESSOR H. A. WILSON, F.R.S.,
KING'S COLLEGE, LONDON.

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VI. *The Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum.*

By Professor H. A. Wilson, *F.R.S., King's College, London.*

Received January 23,—Read February 13, 1908.

The effect of hydrogen on the discharge of negative electricity from hot platinum was examined by the writer in 1903 ('Phil. Trans.,' A, 352, vol. 202, 1903); it was found to produce a very large increase in the current carried by the discharge. At pressures below 0·1 millim. of mercury the leak was found to increase with the pressure and to fall when the pressure was reduced. The experiments in the paper just referred to were all done with nearly new platinum wires which had not been heated in the gas for any great length of time, because it was known that long continued heating caused the wire to disintegrate, its surface becoming covered with a network of cracks. The present paper contains an account of a series of experiments in which wires were heated for long periods in hydrogen, so that any gradual changes in the effect of the hydrogen could be observed. It appears that continued heating in hydrogen alters the character of the effects observed, so that the behaviour of an old wire may be very different from that of a new one.

In the previous paper I suggested that the effect of hydrogen was due to the presence of hydrogen in the surface layer of the platinum, and this view appeared to be supported by the facts. Professor O. W. Richardson ('Phil. Trans.,' A, 413, vol. 207, 1906) puts forward a different theory, viz., that the hydrogen alters the state of the platinum, so that the effect may remain even after the removal of all the hydrogen.

If the wire is heated in oxygen the large leak always immediately disappears, so Professor Richardson supposes that the oxygen destroys the change in the state of the platinum produced by the hydrogen. According to the other view the oxygen burns up the hydrogen present at the surface of the platinum.

The very large increase in the negative leak produced by hydrogen has been recently confirmed by several observers, including O. W. Richardson (*loc. cit.*), F. Horton* and G. H. Martyn.†

Measurements of the current at different temperatures enable the energy required

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* 'Phil. Trans.,' A, 416, 1907.

† 'Phil. Mag.,' August, 1907.

for the liberation of an ion to be calculated. This method of estimating this quantity was first used ('Phil. Trans.,' A, 296, 1901) by the writer to find the energy required to liberate one gram-molecule of ions formed at the surface of hot platinum in air at atmospheric pressure. The mean result then obtained was 60000 calories. RICHARDSON (*loc. cit.*) finds 49200 calories for the same quantity.

It has been suggested that in my experiments the current was very small compared with the saturation current, and that the variation of the current with the temperature was determined by the variation of the velocity of the ions with the temperature and not by the variation of the ionisation. But curves are given in my paper, showing the variation of the current with the E.M.F., which show that 220 volts produced very approximate saturation, and that with 40 volts the current was about one quarter of the saturation current and was then very nearly proportional to the E.M.F. The value 60000 calories was obtained from measurements of the currents due to 40 volts. If the saturation currents, which are also given in my paper, are used instead, the mean result is 50000.

The apparatus used in the present experiments was essentially similar to that employed in the previous investigation. The wire was heated by passing a current through it, and its temperature was estimated by measuring its resistance with a Wheatstone bridge. The wire consisted of a loop of about 11 centims. of wire 0·1 or 0·2 millim. in diameter. The loop was surrounded by an aluminium cylinder contained in a glass tube which could be exhausted. The current from the cylinder to the wire was measured with a galvanometer provided with suitable shunts.

The first part of this paper contains a discussion of the former results with new wires. The paper is divided into the following sections:—

(1) The effect of hydrogen on the leak from new wires.
(2) Variation of the current with the pressure at constant temperature.
(3) Variation of the current with the temperature.
(4) Variation of the current with the time.
(5) The effect of hydrogen on the resistance of the platinum.
(6) Effects due to passing a self-luminous discharge.
(7) A comparison of the negative leak in hydrogen with the positive leak in oxygen.
(8) The theory of the negative leak.
(9) A theory of the variation of the energy necessary for the liberation of an ion with the temperature.
(10) Conclusion.

1. *The Effect of Hydrogen on the Leak from New Wires.*

The variation of the negative leak with the temperature can be represented by the formula $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$, where x denotes the current per square centimetre, θ the absolute temperature, and A and Q are constants.

It was shown in the previous paper that Q and A depend on the pressure of the hydrogen. I propose now to consider this variation of A and Q, and it will be shown that it can be deduced from the assumption that $x = \mathrm{B}p^n$, where p denotes the pressure of the hydrogen, and B and n depend only on the temperature.

The values of A and Q given in the previous paper were calculated from some of the observed currents, and when put in the formula $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$ give nearly the observed values of x. I have recalculated them, using all the observations in turn, and taking the mean of the results. The new values of Q so obtained from the currents and temperatures given in the previous paper differ to some extent from the old values, and since a small error in Q produces a large error in A, the new values of A are considerably different. The following table contains the new values :—

Gas.	Pressure.	Q.	A.
For a Wire Treated with HNO_3 for 24 Hours.			
Air	Small	145000	$1 \cdot 14 \times 10^8$
Wire Boiled in HNO_3 for 1 Hour.			
Air	Small	131000	$6 \cdot 9 \times 10^7$
H_2	0·0013 mm.	110000	10^6
H_2	0·112 ,,	90000	5×10^4
H_2	133 ,,	56000	2×10^2

The new values, of course, represent the results a little better than the old ones.

Any one measurement of the negative leak is subject to a large possible error, but since the values of Q are obtained from a considerable number of observations, it is probable that the effects of errors are to some extent eliminated in the values of Q. For this reason I have attempted to establish the relation between the leak and the pressure by means of the values found for Q and A.

The results given in the previous paper (*loc. cit.*) on the variation of the leak with the pressure of the hydrogen show that the leak is proportional to a power of the pressure less than unity.

In fig. 1 the logs of the pressures and currents given on p. 265 are plotted, and the points fall nearly on a straight line, the slope of which shows that the current varies as $p^{0 \cdot 75}$ nearly.

Let x denote the current per square centimetre of platinum, then at each constant temperature assume $x = \mathrm{B}p^n$, where p denotes the pressure of the hydrogen and B and n depend only on the temperature. This is to be consistent with $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$, where θ denotes the absolute temperature and A and Q depend only on the pressure.

Hence A must be equal to Kp^{-c}, and Q must be equal to $P-2\alpha \log p$, where K and P are constants. Also $n = \alpha\theta^{-1}-c$.

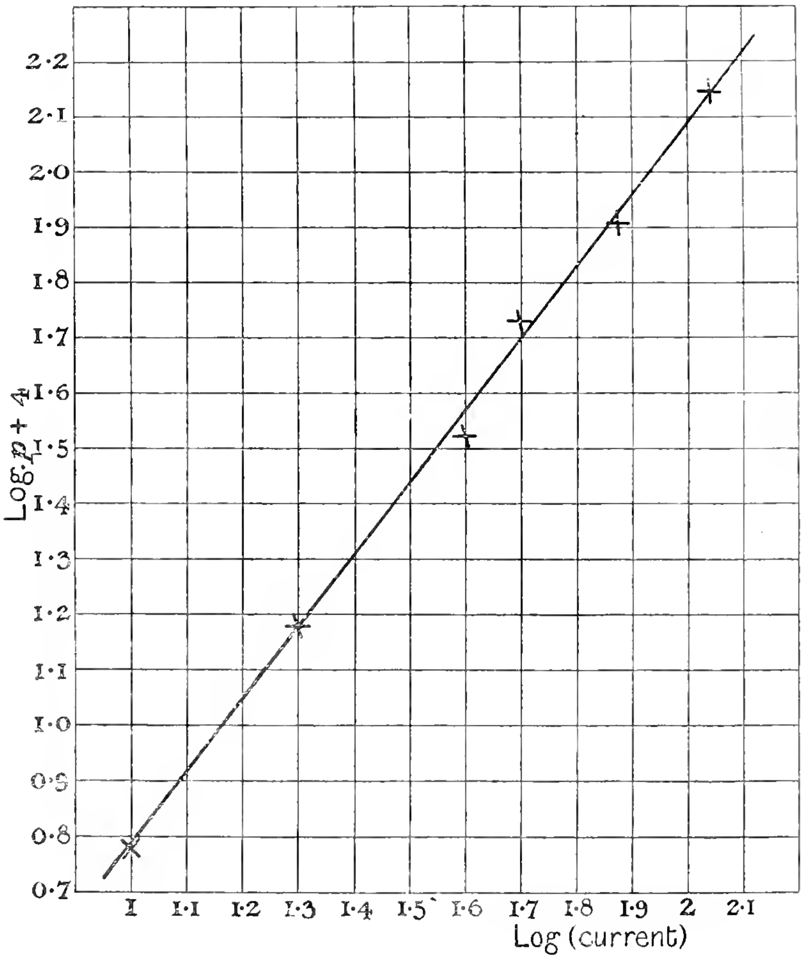

Fig. 1.

The following table contains values of Q calculated from the results given in the previous paper, together with $Q+2\alpha \log p$, taking $\alpha = 2400$.

p.	Q.	$Q+2\alpha \log p$.
millims.		
0·0013	110000	78000
0·112	90000	79500
133	56000	79500

It will be seen that $Q+2\alpha \log p$ is nearly constant, so that we have

$$Q = 79000-2\alpha \log p.$$

It appears therefore that the observed variation of Q with p agrees very well with that calculated on the assumption that $x = Bp^n$ at constant temperature.

Since $n = 0{\cdot}75$ at 1350° C., and $\alpha = 2400$, we have $c = \alpha\theta^{-1}-n=0{\cdot}73$, so that A varies inversely as $p^{0{\cdot}73}$.

The following table is calculated from the results given in the previous paper :—

p.	A.	$Ap^{0\cdot73}$.
millims.		
0·0013	10^6	7800
0·112	5×10^4	10100
133	2×10^2	3600

Thus, while p is increased 10^5 times, $Ap^{0\cdot73}$ only varies by a factor of 3. Only the order of magnitude of A can be obtained from the experimental results, so that it appears that the observed variation of A with p is consistent with the equation $Ap^{0\cdot73}$ = constant.

The equations $A = Kp^{-c}$ and $Q = P-2\alpha\log p$ give $A = Ke^{\frac{c}{2\alpha}(Q-P)}$.

Putting $P = 79000$, $\alpha = 2400$, $K = 9000$, and $c = +0{\cdot}73$, and calculating Q from the values found for A, the following results are obtained :—

$$Q = 6580 \log A + 19100.$$

Gas.	Pressure.	A.	Q (calculated).	Q (found).
	millims.			
Air	—	$1\cdot14\times10^8$	142000	145000
Air	—	7×10^7	138000	131000
H_2	0·0013	10^6	110000	110000
H_2	0·112	5×10^4	90300	90000
H_2	133	2×10^2	54000	56000

It appears, therefore, that this relation is satisfied by the values of A and Q for a wire in air as well as by those for a new wire in hydrogen.

If we put $p = 0$ in the equations $Q = P-2\alpha\log p$ and $A = Kp^{-c}$, we get $Q = \infty$ and $A = \infty$. These equations therefore require modifying to enable them to represent all the values of A and Q. If we suppose $A = A_0/(1+ap^c)$, where a is a constant, then, when ap^c is large compared with unity, this formula will agree with $A = Kp^{-c}$, and when $p = 0$, it gives $A = A_0$.

We have $K = A_0/(1+a)$, which gives $a = 1{\cdot}27\times10^4$. When $p = 0{\cdot}001$, $ap^c = 100$, so that even at this pressure the present formula differs from $A = Kp^{-c}$ only by one per cent.

Since $A = A_0e^{\frac{c}{2\alpha}(Q-Q_0)}$, we get $Q = Q_0-2\alpha c^{-1}\log(1+ap^c)$. This formula gives $Q = Q_0$ when $p = 0$, and for all measurable values of p does not differ appreciably from $Q = Q_0-2\alpha\log p-2\alpha c^{-1}\log a$. When $p = 1$, $Q = P$, so that this is the same as

$Q = P-2\alpha \log p$, which has been shown to agree with the observed values of Q at different pressures.

Since $n = \alpha\theta^{-1}-c$ at the temperature $\theta = \alpha/c$, the leak should be independent of the pressure.

If we substitute the expressions found for A and Q in the equation $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, we get

$$x = A_0(1+ap^c)^{(\alpha/\theta c-1)}\theta^{\frac{1}{2}}e^{-Q_0/2\theta}.$$

If

$$R' = Q_0+2(\theta-\alpha c^{-1}) \log (1+ap^c)$$

and

$$D' = A_0(1+ap^c)^{(\alpha/\theta c-1)},$$

this takes the forms

$$x = A_0\theta^{\frac{1}{2}}e^{-R'/2\theta} \quad \text{and} \quad x = D'\theta^{\frac{1}{2}}e^{-Q_0/2\theta}.$$

In the equation $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, which represents the variation of the leak with the temperature, Q is usually taken to be the energy required for the liberation of one gram-molecule of electrons, while A is proportional to the total number of free electrons present per cubic centimetre in the surface layer of the platinum. The experiments show that Q and A are both diminished by hydrogen. If we suppose that R denotes the true value of the energy required for the liberation of one gram-molecule of electrons, and that this quantity is a function of both θ and p, then, for example, if $R = R'$, we have $x = A_0\theta^{\frac{1}{2}}e^{-R'/2\theta}$, and this equation shows that all the results with new wires can be represented by supposing that the true value of A is A_0, whatever the temperature and pressure. On the other hand, if we denote the true value of A by D, then, for example, if $D = D'$, we have $x = D'\theta^{\frac{1}{2}}e^{-Q_0/2\theta}$, which shows that all the results can be represented by supposing that D is a function of θ and p, while R is always equal to Q_0.

In general, if $R = f(\theta, p)$, where $f(\theta, p)$ denotes a function of θ and p, then D will be given by the equation

$$\log \frac{D}{A_0} = \frac{1}{2\theta}(R-Q)+\left(\frac{\alpha}{\theta c}-1\right) \log (1+ap^c),$$

so that, in general, both D and R may be any functions of θ and p which satisfy this equation, and the observed results will still be represented equally well by the equation $x = D\theta^{\frac{1}{2}}e^{-R/2\theta}$ at any pressure and temperature.

It appears, therefore, that on the view that R and D may be functions of θ as well as of p the results considered so far are not sufficient to determine the values of either of these quantities.

Let x denote the leak in air and x' that in hydrogen at the same temperature; then we have

$$x'/x = (1+ap^c)^{(\alpha/\theta c-1)}.$$

At 900° C. in hydrogen at 26 millims. pressure RICHARDSON (*loc. cit.*, p. 45) found x'/x to be 4×10^8. The above equation gives $x'/x = 2 \times 10^9$. Since a small error in c produces a large error in x'/x, the agreement in this case is as good as could be expected. Thus, if we take $c = 0{\cdot}78$ instead of 0·73, we get $x'/x = 3 \times 10^8$. At 1570° C. in hydrogen at 760 millims. pressure, G. H. MARTYN (*loc. cit.*, p. 309) found $x'/x = 4{\cdot}4 \times 10^4$. The above formula gives $x'/x = 6{\cdot}5 \times 10^4$. At 1343° C. in hydrogen at 0·0013 millim. I found $x' = 5 \times 10^{-8}$. Taking $A_0 = 1{\cdot}14 \times 10^8$ and $Q_0 = 143000$, we get $x = 3 \times 10^{-10}$ at this temperature. Hence $x'/x = 170$. The formula gives $x'/x = 122$.

It appears, therefore, that the formula represents the observed values of x'/x as well as could be expected at pressures from zero to 760 millims., and at temperatures from 900° C. to 1600° C. Within these limits x'/x varies by a factor of more than 10^8.

It should be observed that the results so far considered are those obtained with new wires, and in each case, before measuring the current, some time was allowed to elapse to enable the wire to get into equilibrium with the hydrogen.

The agreement of the formulæ obtained with the observations shows that the equation $x = Bp^n$, which was assumed at the start, is approximately true.

If p is not less than 0·001 millim., the formula for x'/x is approximately $x'/x = a^{(\alpha/\theta c-1)}p^{(\alpha/\theta-c)}$, so that x' varies as a power of the pressure. The following table gives the values of $\alpha\theta^{-1}-c$ at several temperatures, and some values of the power of the pressure calculated directly from recorded observations.

Temperature.	$\alpha\theta^{-1}-c$.	Observed.	Observer.
° C.			
800	1·50	1·12* at 860°	O. W. R.
1000	1·15	—	—
1200	0·90	0·22* at 1181°	O. W. R.
1400	0·70	0·75 at 1350°	H. A. W.
1600	0·55	0·57 at 1490°	H. A. W.
1800	0·43	0·6 at 1550°	H. A. W.

The number 0·22 calculated from RICHARDSON'S results at 1181° C. does not agree with $\alpha\theta^{-1}-c$. This is probably due to the wire not being new. After a wire has been heated a long time in hydrogen at high pressures it may take a very long time for the current to rise after the pressure has been increased. This is probably the explanation of the small value 0·22.

It should be said that since the formulæ from which the formula for x'/x is derived were shown to agree with the values found for A and Q, it was, of course, certain that the calculated values of x'/x would agree with the observed values if these were taken

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* These numbers are calculated from results given by RICHARDSON (*loc. cit.*).

from the same sets of observations as were used in getting the values of A and Q. It is interesting to find that observations by other observers over a very wide range also agree with the calculated values of x'/x.

The following table gives some values of x'/x calculated from the formula when $p = 1$ millim.

Temperature.	x'/x.	x'.
°C.		amperes per sq. centim.
800	$3 \cdot 4 \times 10^{8}$	$1 \cdot 8 \times 10^{-11}$
1000	$3 \cdot 4 \times 10^{6}$	$6 \cdot 8 \times 10^{-9}$
1200	$1 \cdot 1 \times 10^{5}$	$5 \cdot 1 \times 10^{-7}$
1400	$0 \cdot 9 \times 10^{4}$	$1 \cdot 4 \times 10^{-5}$
1600	$1 \cdot 2 \times 10^{3}$	$2 \cdot 0 \times 10^{-4}$
1800	$2 \cdot 4 \times 10^{2}$	$1 \cdot 6 \times 10^{-3}$

It will be seen that x'/x diminishes rapidly as the temperature rises.

Without making any assumption as to whether the hydrogen changes R or D, or both, we may draw an important inference from the results so far considered if we assume that the effect of the hydrogen is due to its presence in the platinum. Since the effect varies continuously with the pressure at constant temperature, we may conclude that the amount of hydrogen in the surface layer of the platinum varies continuously with the pressure. It follows from this that the hydrogen is in the platinum in a state of solution and not in a state of definite chemical combination. If a definite compound were formed, then the amount of combined hydrogen would be zero when the pressure was below its dissociation pressure, and constant when the pressure was above this. The results obtained with new wires indicate therefore that the hydrogen is in solution in the platinum.

2. *Variation of the Current with the Pressure at Constant Temperature.*

A wire, which had been heated for several hours in hydrogen at pressures up to one atmosphere, was kept at a constant temperature, and the leak observed at a series of pressures from one atmosphere downwards. At each pressure the leak was observed until it became nearly constant. The resistance of the wire at 0° C. was determined from time to time, and its resistance when hot was kept proportional to its resistance at 0° C., so that its temperature was kept nearly constant. The difference of potential used was proportional to the pressure, except at low pressures. The following table contains the results obtained in this way :—

TEMPERATURE 1310° C.

Pressure.	Potential difference.	Current.
millims.	volts	amperes
784	784	168×10^{-8}
385	385	83×10^{-8}
183	184	35×10^{-8}
71	72	26×10^{-8}
46	46	26×10^{-8}
23	30	16×10^{-8}
10	20	36×10^{-8}
0·85	20	78×10^{-8}
0·45	20	60×10^{-8}
0·24	20	46×10^{-8}
0·13	20	38×10^{-8}
0·068	20	40×10^{-8}
0·006	20	40×10^{-8}
0·000	20	40×10^{-8}

It will be seen that below 200 millims. the current does not vary much with the pressure. The rise at 0·8 millim. is probably due to ionisation by collisions. In the previous paper the following results were obtained with new wires :—

TEMPERATURE 1340° C.

Pressure.	Potential difference.	Current.	$\frac{\text{Current}}{\text{Pressure}}$.
millims.	volts	amperes	
766	40	3×10^{-3}	$3{\cdot}9 \times 10^{-6}$
450	40	$1{\cdot}5 \times 10^{-3}$	$3{\cdot}3 \times 10^{-6}$
156	40	$2{\cdot}2 \times 10^{-4}$	$1{\cdot}41 \times 10^{-6}$
14	40	6×10^{-5}	$4{\cdot}3 \times 10^{-6}$
0·11	40	4×10^{-6}	36×10^{-6}
0·0013	40	5×10^{-8}	39×10^{-6}

It ought also to be said that the last two results in this table were obtained with a wire which had never been in hydrogen at more than a small fraction of a millimetre pressure. The first four results were obtained by letting hydrogen in, keeping the temperature constant. Comparing the two tables, we see that there is a surprising difference between them. The first table shows very little variation with the pressure, while the second shows that the leak increased 10^5 times when the pressure was increased 10^6 times.

The difference between the old results and the new ones is so large that it was considered worth while to repeat the old experiments. A new wire was put up and heated in air, and was found to give a small current. The air was then pumped out and small quantities of pure hydrogen were successively admitted. The current was measured at each pressure, keeping the temperature constant. The following table contains the results obtained.

TEMPERATURE 1564° C.

Pressure.	Current.
millim.	amperes
0·006	$2·5 \times 10^{-7}$
0·028	$4·5 \times 10^{-7}$
0·056	$1·8 \times 10^{-5}$
0·337	$5·2 \times 10^{-5}$
0·169	$1·2 \times 10^{-5}$
0·090	$2·4 \times 10^{-6}$
0·003	$5·0 \times 10^{-8}$

The last three pressures were obtained by pumping out the hydrogen.

These results show that with a new wire the leak rises with the pressure and falls when it is reduced. The experiment was repeated immediately, and similar results were obtained. Next day, after the wire had been all night in hydrogen at a low pressure, the following results were obtained:—

Pressure.	Current.
millim.	amperes
0·001	5×10^{-8}
0·017	5×10^{-8}
0·146	2×10^{-7}
0·297	9×10^{-7}
0·618	11×10^{-7}
0·281	11×10^{-8}
0·146	6×10^{-8}
0·073	5×10^{-8}

It appears, therefore, that with a new wire the results are very different from those obtained with an old wire.

If a wire which has been heated in hydrogen at high pressures and is giving a large leak nearly independent of the pressure is heated in air, the leak falls at once to a small value. If the air is pumped out and a little hydrogen admitted, the leak at high temperatures is not affected at first, but after heating in the hydrogen for some time it usually develops rather quickly. The leak then rises when the pressure is increased, and has about the same value as with a new wire. On pumping out the hydrogen the leak only falls very slowly with the time.

The following table gives the currents at several pressures with a wire treated in the way just described. This wire, after heating in air, was heated to 1490° C. in hydrogen at 0·005 millim. pressure. The leak remained unchanged for two hours and then rose to about 4×10^{-6} ampere per square centimetre. After this, on increasing the pressure, the leak rose at once and remained steady.

TEMPERATURE 1490° C.

Pressure.	Current.
millim.	amperes
0·0135	$6 \cdot 56 \times 10^{-6}$
0·0168	$7 \cdot 80 \times 10^{-6}$
0·0281	$10 \cdot 50 \times 10^{-6}$
0·0399	$12 \cdot 70 \times 10^{-6}$
0·0579	$17 \cdot 20 \times 10^{-6}$
0·0776	$20 \cdot 50 \times 10^{-6}$
0·1151	$24 \cdot 60 \times 10^{-6}$

This experiment was repeated several times with similar results. On diminishing the pressure the leak fell off very slowly with the time, so that the pressure could be reduced to nothing without much diminishing the leak. This shows that the increase in the leak is not due to ionisation by collisions.

If the logs of the numbers just given are plotted, the points fall nearly on a straight line, the slope of which shows that the current is proportional to $p^{0·57}$. At 1490° C. $\alpha\theta^{-1}-c$ is equal to 0·63. Thus the variation of the leak with the pressure is nearly that calculated from the old results with new wires. The value of the leak at 1490° C., with $p = 0·1151$, given by the formula obtained in Section 1, is $1·3 \times 10^5$, which does not differ much from the leak found. This wire, therefore, which had been heated in hydrogen at high pressures for a long time and then in air, gave the same leak in hydrogen as a new wire. It differed from a new wire only in that the leak fell very slowly with the time when the pressure was diminished, and that on first admitting the hydrogen the leak did not rise for a considerable time.

If we regard the leak from a wire which has not been heated in hydrogen at a high pressure as due to dissolved hydrogen, then, since in the case just described the leak was the same as that given by a new wire, we must regard the leak in this case also as due to dissolved hydrogen. Thus the difference between an old wire and a new one appears to be that the old wire absorbs and evolves hydrogen much more slowly than the new wire.

A wire which has been heated in hydrogen at high pressures differs from a new wire and from an old wire that has been heated in air. It always gives a very large leak which is nearly independent of the pressure. Even when it is heated in a good vacuum for many hours the leak does not fall.

Professor O. W. RICHARDSON (*loc. cit.*) found that the leak in hydrogen was independent of the pressure when this was reduced from a few millimetres to nearly zero.

His wires, therefore, appear to have had the properties of old wires. He has described some experiments in which a wire giving a leak independent of the pressure was heated for many hours in a good vacuum and a slow evolution of gas was observed. The total volume of gas evolved, measured at 760 millims. pressure, was about 30 times that of the wire. I have repeated this experiment of RICHARDSON'S and have confirmed his result that the leak does not fall even after heating the wire for many hours in hydrogen at a low pressure. In my experiments the wire appeared to cease evolving an appreciable amount of gas after heating for about one hour.

The following table contains some numbers obtained in one series of observations with a wire kept between 1500° C. and 1600° C. The leak at 1600° C. was about 10^{-3} ampere. The wire had previously been heated in hydrogen and was giving a leak very large compared with the air leak. The volume of the apparatus was approximately 1000 cub. centims.

Time.		Pressure.
h.	m.	millim.
10	55	0·0017
12	7	0·0028
16	48	0·0028

In this experiment the pressure did not rise 0·0002 millim. in the last five hours. It seems certain, therefore, that a wire giving a large leak due to its having been heated in hydrogen can be heated to a very high temperature in hydrogen at a very small pressure for several hours without evolving an appreciable amount of gas.

On another occasion a wire was kept at about 1400° C. from 5 P.M. to 10 A.M., and the pressure did not rise more than 0·005 millim., although the wire was giving a large leak, due to its having been heated in hydrogen. If we admit that a wire giving a large leak does not necessarily evolve gas, we may explain this in two ways. Either the wire contains no hydrogen, or it contains hydrogen in a state of very stable combination. In the section of this paper on the effect of hydrogen on the resistance of the wire it is shown that heating in air diminishes the resistance at the same time that it destroys the leak. This seems to show that the surface layers of the wire contain hydrogen which is burnt up by the air. The fact that platinum black absorbs very much more hydrogen than solid platinum also points to the conclusion that the absorption is mainly a surface effect. The presence of hydrogen in a wire can be tested by heating it in oxygen and observing the pressure before and after heating. If hydrogen is present it will form water which will be absorbed by the P_2O_5, and so the pressure will be diminished. RICHARDSON (*loc. cit.*, p. 45) describes an experiment of this kind and observed a diminution in the pressure. In this experiment of RICHARDSON'S a wire at 900° C. in hydrogen at 26 millims. pressure gave a negative leak 4×10^8 times greater than the leak at the same temperature in oxygen. On heating in oxygen the pressure fell from 1·067 millims. to 1·026 millims. I have tried a similar experiment with a wire giving a large leak independent of the pressure which was heated in hydrogen at a small pressure until it ceased to evolve gas. A new wire was put up and heated for a few hours in hydrogen at atmospheric pressure. It was then left cold in hydrogen all night, and in the morning gave a large leak nearly independent of the pressure. The gas was then pumped out till the pressure was 0·0011 millim. The wire was then heated to a temperature of about 1200° C. for four hours, during which time the leak was about 3×10^{-5} ampere, but rose slightly towards the end of the experiment. After one and a-half hours the pressure had risen to 0·01 millim., but it remained constant during the next two and a-half hours. The wire was then allowed to cool, and oxygen was let in to a high pressure and pumped out several times. The oxygen was then pumped out to 0·0015 millim. The wire was then heated for a few seconds to about 1100° C., and after ten minutes the pressure was 0·0012 millim. The wire was then heated for two minutes and after a time the pressure fell to 0·0009 millim. The wire was now heated for two minutes to about 1500° C., and after a time the pressure was again 0·0009 millim.

On first heating the wire in the oxygen a large leak was observed which very quickly fell to a very small value. The capacity of the apparatus in the above experiment was 500 cub. centims., so that the volume of hydrogen (measured at 760 millims.) contained in the wire was 8×10^{-3} cub. centim. The volume of the wire was $10 \times \frac{22}{7} \times \frac{1}{(100)^2} = 3 \times 10^{-3}$ cub. centim., so that the wire contained about three times its volume of hydrogen, although it had been heated for two and a-half hours without evolving any gas. The gas evolved during the first one and a-half hours may have come from the wire, but some of it probably came from the surrounding electrode, which, of course, got warm during the long continued heating. When the wire was heated in oxygen, the electrode was not heated appreciably, because the current was only kept on a short time. I think this experiment shows that a wire which has ceased to evolve hydrogen when heated in hydrogen at a small pressure may still contain several times its volume of hydrogen.

If the wire absorbed oxygen when heated in it this would account for the fall in the pressure. The oxide of platinum, PtO, which is formed at 510° C., decomposes completely at 560° C. The temperature in the above experiment was much higher than 560° C., so that it is not likely that any oxide was formed. According to Bodländer, platinum absorbs oxygen energetically at from 700° C. to 900° C., but these temperatures are also lower than the temperature used.

If we admit that a wire giving a large leak independent of the pressure contains hydrogen, to which the leak is due, then it is necessary to suppose that the hydrogen is not all merely dissolved in the platinum. Since the leak is independent of the pressure, the amount of hydrogen in the wire must be independent of the pressure. If the temperature of the wire is raised while it is in a good vacuum, the leak on cooling to the original temperature is often a little lower than before. After standing cold the leak is usually higher on first heating the wire, and then falls off quickly at first and then more slowly. I think these variations may be ascribed to hydrogen dissolved in the wire like that in a new wire. The leak does not fall below a certain value at a given temperature, however long the wire is heated in a vacuum, even if the temperature is raised and lowered. RICHARDSON's experiments show this very clearly, and I have confirmed this result. Very often the leak rises slightly while the wire is being heated in hydrogen at a very low pressure. To explain these results on the theory that the large leak is due to hydrogen contained in the surface layer of the platinum, it is necessary to suppose that a very stable compound of hydrogen and platinum is formed in the surface layer which has a dissociation pressure less than about 0·002 millim. even at high temperatures. In addition to the combined hydrogen the wire may contain dissolved hydrogen, but this will be got rid of by heating in a vacuum. The absorption of hydrogen by platinum at high temperatures has been investigated by several people, and they have all found that part of the gas can be driven off by heating in a vacuum, while part cannot be driven off in this way. It should be observed that the pressure of the hydrogen is never really reduced to zero by pumping out. It is possible that by reducing the pressure sufficiently the combined hydrogen could be removed, but if it has a finite dissociation pressure this must be very small.*

I think, therefore, that the difference between a new wire and a wire which has been heated in hydrogen at a high pressure is mainly due to the presence of combined hydrogen in the latter.

When the combined hydrogen has been burnt out of an old wire by oxygen the wire gives the same leak in hydrogen at a low pressure as a new one, but the leak takes a long time to appear and does not fall much when the pressure is reduced. This seems to show that the old wire only dissolves the hydrogen very slowly. Continued heating in hydrogen and air appear, therefore, to produce a change in the state of the platinum. This change of state does not appear to affect the final value of the leak, and is not destroyed by heating in oxygen, which at once destroys the leak.

This change of state may very likely be due merely to long continued heating; it probably consists of an alteration of the crystalline structure of the platinum. The formation of a compound of platinum and hydrogen in the surface layer, and its subsequent destruction by oxygen, might be expected to produce a change in the state of molecular aggregation of the platinum. Another thing which may have something to do with this change of state is the slow evaporation of the wire at high temperatures.

In my paper on the electrical conductivity of air and salt vapours ('Phil. Trans., A,' 1901) I observed that the leak from hot platinum in air falls off during long continued

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[*Added March 20, 1908.—Since writing the above I have found that on heating to above 1600° C. at a very low pressure the large leak rapidly disappears.]

heating, at first rapidly and then much more slowly, and I suggested that this was due to a change in the state of molecular aggregation of the platinum. The platinum in these experiments was heated by a coal-gas flame and so no doubt contained hydrogen, so that this effect was probably due to the same cause as that just described.

3. *Variation of the Current with the Temperature.*

The leak from wires which had been heated in hydrogen at high pressures and were giving a leak independent of the pressure was measured at a series of temperatures on several occasions. The following table contains a set of results obtained in this way at a pressure of 0·003 millim.

Temperature.	Current.
° C.	ampere per sq. centim.
1578	$9 \cdot 51 \times 10^{-5}$
1613	$19 \cdot 26 \times 10^{-5}$
1648	$38 \cdot 7 \times 10^{-5}$
1683	$72 \cdot 3 \times 10^{-5}$

The mean values of A and Q in the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$ calculated from the above results are $A = 1 \cdot 67 \times 10^{10}$ and $Q = 135300$, and with these values the formula represents the observations very well.

The value of Q for a new wire in air is probably about 135000, so that Q for an old wire in hydrogen is nearly the same as for a new wire in air.

With the same wire, about a month later, the following results were obtained. The wire was heated in air, which was then pumped out and hydrogen was let in to a small pressure. After a time a leak developed which increased with the pressure. After heating for several hours at low pressures, hydrogen was let in to 0·084 millim. pressure. The leak then rose, but became constant after one hour. At each temperature the leak was then steady.

PRESSURE 0·084 millim.

Temperature.	Current.
° C.	ampere per sq. centim.
1265	$6 \cdot 8 \times 10^{-7}$
1377	$51 \cdot 0 \times 10^{-7}$
1496	$317 \cdot 0 \times 10^{-7}$

These numbers give $Q = 89000$ and $A = 6 \times 10^{4}$. The formulæ $A = Kp^{-c}$ and $Q = P - 2\alpha \log p$ obtained in Section 1 give $A = 5 \cdot 5 \times 10^{4}$ and $Q = 83000$ at this pressure. The leak obtained in this experiment was nearly the same as with a new wire at the same pressure. This confirms the conclusion that an old wire after heating in air gives the same leak in hydrogen as a new wire, although the current takes much longer to get to its final value at any pressure.

The results obtained with the wire after heating in hydrogen at a high pressure are quite different from those given by a new wire. The values of A and Q, $1 \cdot 67 \times 10^{10}$ and 135300, obtained do not satisfy the relation $A = A_0 e^{c(Q-Q_0)/2\alpha}$, which has been shown to hold for all the other values of A and Q.

According to the view suggested in the last section, the wire after heating for some time in hydrogen at a high pressure contains a stable compound of platinum and hydrogen having a dissociation pressure less than 0·002 millim. The amount of combined hydrogen is consequently independent of the pressure.

The amount of combined hydrogen must be independent of the temperature as well as of the pressure. For if on raising the temperature some of it escaped, this would show that its dissociation pressure was greater than that of the hydrogen outside, and so the whole of the compound would decompose. But a wire giving a large leak independent of the pressure can be heated in a good vacuum to 1400° C. without the leak falling; hence, at any rate below this temperature, the amount of combined hydrogen must be independent of the temperature.

Since Q for a wire containing combined hydrogen is nearly the same as Q for a new wire in air, it follows that the ratio of the leaks should be independent of the temperature. The following table contains the values of the leak given above and those for a new wire in air taken from my previous paper.

New wire in air.		Old wire.		
Temperature.	Leak.	Temperature.	Leak.	Ratio.
° C.		° C.		
1686	4×10^{-8}	1683	$7 \cdot 23 \times 10^{-4}$	$1 \cdot 81 \times 10^{4}$
1651	2×10^{-8}	1648	$3 \cdot 87 \times 10^{-4}$	$1 \cdot 93 \times 10^{4}$
1616	1×10^{-8}	1613	$1 \cdot 93 \times 10^{-4}$	$1 \cdot 93 \times 10^{4}$

It will be seen that the ratio is nearly constant.

The leak from wires which had been heated in hydrogen was measured in air at various temperatures many times during the course of this investigation. The leaks obtained were of the same order of magnitude as those given in the previous paper for new wires in air. They were from 2 to 10 times greater than the leak given in the previous paper for a wire which had been treated with nitric acid for 24 hours. One wire, which had been used a long time in hydrogen, was made the positive electrode in HNO_3 for several hours, and was then heated in air at a small pressure. It was found to give nearly the same leak as that from the wire just mentioned.

4. *Variation of the Current with the Time.*

In the previous paper the variation of the current with the time was considered in detail, and it was shown that the results obtained could be explained by supposing that the leak depended on the amount of hydrogen in the wire, and that a considerable time was required for the hydrogen in the wire to get into equilibrium with that outside. For example, it was shown that on diminishing the pressure at constant temperature the leak fell slowly. The previous results were obtained with new wires. With wires which have been heated in hydrogen at high pressures the variation with the time is similar to that with new wires, but the leak does not fall below a certain value, however much the pressure is reduced. The following table contains a series of observations on a wire at 1310° C. in hydrogen. The wire was left cold during each night.

Time.		Current.	Potential difference.	Pressure.
Days.	Minutes.			
		ampere	volts	millims. of Hg.
0	0	$8 \cdot 6 \times 10^{-5}$	200	195
	10	$4 \cdot 4 \times 10^{-5}$	200	195
	35	$4 \cdot 5 \times 10^{-5}$	200	195
	100	$5 \cdot 2 \times 10^{-6}$	200	195
1	0	$8 \cdot 4 \times 10^{-5}$	784	784
	10	$2 \cdot 8 \times 10^{-5}$	784	784
	50	$9 \cdot 5 \times 10^{-6}$	784	784
	100	$2 \cdot 8 \times 10^{-6}$	784	784
2	0	$3 \cdot 5 \times 10^{-6}$	784	784
	100	$1 \cdot 5 \times 10^{-6}$	784	784
	120	$1 \cdot 5 \times 10^{-6}$	784	784
	130	$7 \cdot 0 \times 10^{-7}$	385	385
	180	$7 \cdot 4 \times 10^{-7}$	385	385
	220	$1 \cdot 3 \times 10^{-7}$	30	23
3	0	$7 \cdot 5 \times 10^{-7}$	30	23
	60	$1 \cdot 9 \times 10^{-7}$	30	23
	200	$3 \cdot 4 \times 10^{-7}$	30	0·84
4	0	$6 \cdot 2 \times 10^{-7}$	20	0·84
	60	$5 \cdot 4 \times 10^{-7}$	20	0·84
	120	$5 \cdot 6 \times 10^{-7}$	20	0·84
5	0	$4 \cdot 4 \times 10^{-7}$	20	0·24
	60	$3 \cdot 5 \times 10^{-7}$	20	0·24
	180	$3 \cdot 5 \times 10^{-7}$	20	0·24
	300	$3 \cdot 6 \times 10^{-7}$	20	0·000
6	0	$3 \cdot 2 \times 10^{-7}$	20	0·006
	60	$3 \cdot 6 \times 10^{-7}$	20	0·006
9	0	$3 \cdot 8 \times 10^{-6}$	20	1·64
	60	$3 \cdot 7 \times 10^{-7}$	20	1·64
	120	$5 \cdot 0 \times 10^{-7}$	40	1·64

The wire was left cold between the seventh and tenth days. After several weeks' further experimenting with this wire at various temperatures and pressures, the leak at the same temperature as that at which the above results were obtained was

2×10^{-7}, and almost independent of the pressure. It will be seen that the leak fell rapidly at first and was usually greater after leaving the wire cold all night. It was nearly independent of the pressure below 200 millims. The variation of the leak with the time can usually be represented roughly by a formula of the type $Ae^{-at} + Be^{-\beta t} + C$, in which α is much greater than β, and A greater than B or C. The term C represents the final value of the leak, which is nearly constant, but it also falls off very slowly. The term Ae^{-at} represents the large leak at first, and falls to half value in from a few seconds to 20 minutes, according to the temperature and state of the wire. The second term falls to half value in several hours. Irregular variations in the leak sometimes take place which make it impossible to determine α and β exactly. Moreover, these quantities are not the same on different occasions, but depend greatly on the previous treatment of the wire.

I think these facts indicate that the wire absorbs hydrogen in the cold, and that part of this hydrogen is given off fairly rapidly on heating, part is given off very slowly, and part not given off at all, even in a vacuum

If an old wire which has been heated in hydrogen for a long time is heated in air, and then again to a very high temperature (above 1600° C.) in hydrogen, the leak is nearly the same in hydrogen as in air. On reducing the temperature the leak remains small for a time, but then begins to increase rapidly and after a time gets to about the usual value for a wire in hydrogen. At first, while the leak is increasing with the time, it falls when the temperature is raised. After further heating the leak becomes more steady, and then always rises with the temperature. These facts seem to show that an old wire does not absorb hydrogen above a certain temperature, or only does so very slowly.

The fact that while the leak is rising with time it falls on raising the temperature is difficult to explain. This effect was obtained on several separate occasions. The leak, then, has a definite maximum value at a certain temperature. The leak in these experiments was saturated, so that the decrease on raising the temperature was not due to a diminution in the velocity of the ions. The leak rose when the temperature was diminished. In one experiment the current was 10^{-7} ampere at 1300° C., 4×10^{-7} at 1400° C., and 4×10^{-8} at 1500° C.

An increase in the leak while heating in hydrogen at constant temperature is usually accompanied by a small fall in the pressure, showing that the wire has absorbed hydrogen. Much weight cannot be given to observations showing a small change in the pressure, because small quantities of gas may be evolved or absorbed by the glass or the electrodes, so that a small change in the pressure is not necessarily due to gas evolved or absorbed by the wire.

One wire which gave a large leak in hydrogen when it was new, after heating in hydrogen for several days was heated in air and then gave the usual small air leak. On again heating in hydrogen to above 1600° C. for ten hours the leak remained small and showed no signs of rising with time.

5. *The Effect of Hydrogen on the Resistance of the Platinum.*

It is well known that when platinum is saturated with hydrogen its resistance is increased by a small amount. It was thought that this effect might be employed as a test of the presence of hydrogen in the wire. A wire which had been heated for some time in hydrogen and which gave a large leak independent of the pressure was used. It was heated for some hours in a very good vacuum and still gave the same current as in hydrogen at several millimetres pressure. Its resistance at 0° C. was then carefully determined and it was then heated to 1400° C. for a few seconds in air. The leak immediately fell to the air value. The resistance at 0° C. was again determined and was about one part in a thousand less than before. On again heating in hydrogen the resistance rose again.

This experiment shows that the increase in the resistance due to hydrogen is probably a purely surface effect, for oxygen does not diffuse into platinum. If we regard the increase in the resistance as due to the formation of the compound discussed in Section 2, then it is necessary to suppose that this compound is only formed in the surface layer of the platinum. It is well known that finely divided platinum absorbs much more hydrogen than platinum in large pieces, which also suggests that the compound formed is confined to the surface. The effect of the hydrogen on the negative leak is, of course, a surface effect and so depends only on the state of the surface layer.

6. *Effects due to Passing a Self-Luminous Discharge between the Wire and surrounding Electrode.*

After heating an old wire in air it gives a very small leak in hydrogen, at any rate for a time. If, while it is giving a very small leak, a luminous discharge is passed between the wire and the surrounding electrode by means of a large battery of cells, the leak on stopping the discharge is enormously increased. If the discharge is only passed for a few seconds, a moderate increase can be obtained, and then the leak has a maximum value at a certain temperature. After passing the discharge for some minutes the leak obtained always rises with the temperature.

These effects, it will be seen, are very similar to the effects observed during the increase of the leak when an old wire which had been heated in air was heated to a moderate temperature in hydrogen. The discharge appears to accelerate the recovery of the leak. The maximum value of the leak was obtained both with rising and falling temperatures. The current was nearly independent of the potential difference in all these experiments. This was tested specially at every temperature by taking two measurements with different potentials. The maximum value is, therefore, not due to the currents at the higher temperatures not being saturated. I hope to make further experiments on these effects.

7. *A Comparison of the Negative Leak in Hydrogen with the Positive Leak in Oxygen.*

The positive leak in oxygen has been studied very fully by Professor O. W. RICHARDSON ('Phil. Trans.,' A, 413, 1906), who attributes it to the presence of oxygen in the surface layer of the wire, and this view is undoubtedly in accordance with the facts. I attribute the negative leak in hydrogen in the same way to the presence of hydrogen in the surface layer of the platinum. If this view is correct, the behaviour of the positive leak in oxygen might be expected to be closely analogous to the behaviour of the negative leak in hydrogen. As a matter of fact, there is an extremely close analogy between the two, as will be shown presently.

In my previous paper I showed that treating a wire with nitric acid and heating it in air diminished the negative leak to a value very small compared with that usually obtained on heating a wire in a vacuum. This diminution was explained as being due to the removal of traces of hydrogen or other substances from the wire, and I suggested that possibly a complete removal of such traces would entirely destroy the negative leak. Since then RICHARDSON (*loc. cit.*) has described an experiment in which the leak from a platinum tube in air at atmospheric pressure was measured while hydrogen was allowed to diffuse through the platinum from the inside of the tube out into the air. He found that the small negative leak was unchanged by the hydrogen. I have repeated this experiment and confirmed his result. As RICHARDSON points out, this experiment shows clearly that the very small negative leak given by platinum in air is not due to traces of hydrogen in the platinum. In addition, measurements of the negative leak from clean platinum wires in air and other gases, except hydrogen, give fairly concordant results, so that I think there is now no doubt that there is a small negative leak due to the platinum itself. In fact, since traces of hydrogen in the surface of the platinum must be burnt up at once when it is heated in air, it is almost impossible that such traces could be the cause of the small leak given in air. This conclusion, of course, does not apply to the much larger leaks which are obtained when an ordinary platinum wire is heated in a vacuum without any special precautions. I think there is no doubt that they are due, as I suggested, to traces of hydrogen. In the present paper, when the negative leak in hydrogen is referred to, it is not intended to imply that there is not a small negative leak due to the platinum itself.

To return to the comparison of the positive and negative leaks, the variation with the pressure at constant temperature will be taken first. RICHARDSON shows that the positive leak increases with the pressure of the oxygen at low pressures rapidly, but at high pressures more slowly. The relation between the leak and the pressure is $x = \alpha p^n/(\beta+p^n)$, where α, β, and n are constants. The constant n varies with the temperature, being $\frac{1}{2}$ at 820° C. and 1 at 1170° C. Assuming that the leak depends on the amount of oxygen in the surface layer of the platinum, this shows that the oxygen dissolves in the platinum at low pressures, while at high pressures—since the leak becomes nearly independent of the pressure—there is an indication of chemical combination.

It will be seen that these results are very analogous to the results obtained with the negative leak in hydrogen. This increases proportionally to a power of the pressure at first, but in the course of time a compound is formed, and the leak is then nearly independent of the pressure. The difference between the two cases is that the positive leak always gets to a definite value at any pressure if enough time is allowed. This means that the compound formed can easily dissociate. The negative leak at first, before the stable compound is formed, exhibits hysteresis effects, that is, it lags behind changes in the pressure. RICHARDSON finds precisely the same thing with the positive leak, and it is almost certainly due in each case to the gas in the wire taking time to get into equilibrium with that outside.

The negative leak is often large on first heating a wire, and falls off with the time. The same thing applies to the positive leak, and in each case it is almost certainly due to the escape of gas absorbed while the wire was cold. The variation of both leaks with the temperature is represented by the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$.

I think, therefore, that the negative leak in hydrogen bears the same relation to the hydrogen that the positive leak in oxygen does to the oxygen. If one of them is due to the presence of the gas in the surface layer of the wire, then the other is also. The precise manner in which the presence of hydrogen in the surface layer alters the negative leak will be considered in Section 9.

8. *The Theory of the Negative Leak.*

Professor O. W. RICHARDSON ('Phil. Trans.,' A, 343, 1903) has given a very simple and elegant theory of the negative leak from hot bodies. According to this theory the metal contains electrons which move about freely inside the metal and have a velocity distribution like the molecules of a gas. Those electrons which collide with the surface with a normal velocity greater than a certain value escape. This theory leads to the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$, and according to it A is proportional to the number of free electrons per cubic centimetre in the metal. According to this theory A ought to be nearly independent of the pressure and nature of the gas present, because the electrical conductivity of the metal is very little affected, even by hydrogen.

In my previous paper I showed that hydrogen changed the value of A by a very large factor, and therefore I suggested that RICHARDSON's theory required modification in order to enable it to account for the facts.

It is shown in Section 1 of the present paper that if the true values of Q and A are denoted by R and D, and if we suppose that R and D may be functions of the temperature θ as well as of the pressure, then the variations of Q and A can be explained either by supposing that D is constant and R a function of θ and p, or that

R is constant and D a function of θ and p. Let us suppose, then, that D is constant, which is in accordance with RICHARDSON's theory. We have, then,

$$R = Q + 2\theta \log (D/A).$$

According to this equation R increases uniformly with the temperature, and R cannot be calculated unless D is known. To determine D it is necessary to make some hypothesis to explain the variation of R with the pressure and temperature. This is done in the next section.

The negative leak from lime can, like that from platinum, be represented by the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$; and Dr. HORTON ('Phil. Trans.,' A, 1907) has shown that the electrical conductivity of lime at high temperatures can also be represented by a formula of the same type. He concludes that the number of free electrons per cubic centimetre of lime must increase rapidly with the temperature, so that, if A in the formula giving the negative leak were proportional to the number of electrons, then A ought to increase rapidly with the temperature. Dr. HORTON found A to be nearly independent of the temperature, and hence concluded that A was not proportional to the number of free electrons per cubic centimetre. It is easy to show that this conclusion is not really required by the results, which can be reconciled as follows:— Let N denote the number of free electrons per cubic centimetre of lime, and suppose that the electrical conductivity is proportional to $N\theta^{\frac{1}{2}}$, so that N varies as $e^{-Q'/2\theta}$, where Q′ is the value in the formula giving the conductivity.

Suppose the negative leak from lime is given by the formula $x = D\theta^{\frac{1}{2}}e^{-R/2\theta}$; then, according to RICHARDSON's theory, D varies as N, which varies as $e^{-Q'/2\theta}$. Hence we get $D = Ae^{-Q'/2\theta}$, where A is a constant, which gives

$$x = Ae^{-Q'/2\theta}\theta^{\frac{1}{2}}e^{-R/2\theta}.$$

The quantities found by Dr. HORTON are, therefore, A and Q′+R, and the independence of A and the temperature agrees with RICHARDSON's theory if the assumptions here made are allowed.

9. *A Theory of the Variation of* R *with the Temperature.*

To explain the energy necessary to enable an electron to escape from the platinum, we may suppose that an electrical double layer exists at the surface. Let this consist of an infinitely thin layer of electricity at a distance t from the platinum, having a charge σ per square centimetre. If no electrons were present, the difference of potential between the layer and the platinum would be $4\pi\sigma t$; but, actually, electrons will be present in between the layer and the platinum and will increase the electric force. This effect will increase as the temperature rises, so that if R is due to such a layer it will vary with the temperature.

Let n denote the number of electrons per cubic centimetre at a point at a distance x

from the platinum surface. Let p denote the gas pressure due to the electrons and let ρ denote the electric volume density, so that $\rho = ne$. Then, when there is equilibrium, we have $-dp/dx + \mathrm{F}\rho = 0$, where F denotes the electric force inside the layer. Outside the layer, in the same way, $-dp/dx + \mathrm{F}'\rho = 0$, where F′ denotes the force outside. Then at the layer $x = t$ and $\mathrm{F}_t + 4\pi\sigma = \mathrm{F}'_t$; also, since ρ must be continuous and $d\mathrm{F}/dx = 4\pi\rho$, we have $d\mathrm{F}/dx_t = d\mathrm{F}'/dx_t$.

At a great distance from the platinum we have for equilibrium $\mathrm{F}' = 0$ and $d\mathrm{F}'/dx = 0$, and at $x = 0$, $d\mathrm{F}/dx = 4\pi\rho_0$, where $\rho_0 = n_0 e$ and n_0 denotes the number of electrons per cubic centimetre in the platinum. These relations enable V, the difference of potential between the layer and the platinum, to be calculated.

Let $p = -\beta\rho$, where β is a constant at constant temperature, so that

$$-\frac{dp}{dx} = \beta\frac{d\rho}{dx} = \frac{\beta}{4\pi}\frac{d^2\mathrm{F}}{dx^2}.$$

Hence

$$\beta\frac{d^2\mathrm{F}}{dx^2} + \mathrm{F}\frac{d\mathrm{F}}{dx} = 0,$$

which gives

$$\beta\frac{d\mathrm{F}}{dx} + \tfrac{1}{2}\mathrm{F}^2 = c.$$

In the same way

$$\beta\frac{d\mathrm{F}'}{dx} + \tfrac{1}{2}\mathrm{F}'^2 = c' = 0.$$

Hence

$$-\frac{\beta}{\mathrm{F}'} = -\frac{x}{2} + \text{constant},$$

which gives

$$\beta\left(\frac{1}{\mathrm{F}'} - \frac{1}{\mathrm{F}'_t}\right) = \tfrac{1}{2}(x-t).$$

When $x = 0$, we have $4\pi\rho_0\beta + \frac{1}{2}\mathrm{F}_0^2 = c$, and when $x = t$, since

$$\frac{d\mathrm{F}}{dx_t} = \frac{d\mathrm{F}'}{dx_t} = -\frac{\mathrm{F}'^2_t}{2\beta},$$

we get $\mathrm{F}_t^2 - \mathrm{F}'^2_t = 2c$, or $\mathrm{F}_t^2 - (\mathrm{F}_t + 4\pi\sigma)^2 = 2c$, which gives $\mathrm{F}_t = -c/4\pi\sigma - 2\pi\sigma$. Now in the case of hot platinum we know that only a very small fraction of the electrons which collide with the surface escape, so that ρ outside the layer is very small; hence, when t is small and σ large, it is clear that F'_t will be small compared with F_t. Consequently $\mathrm{F}_t^2 = 2c$ very nearly, so that $2c = (-c/4\pi\sigma - 2\pi\sigma)^2$, which gives $c = 8\pi^2\sigma^2$, so that $\mathrm{F}_t = -4\pi\sigma$. Hence

$$\beta\frac{d\mathrm{F}}{dx} + \tfrac{1}{2}\mathrm{F}^2 = 8\pi^2\sigma^2.$$

Integrating this gives

$$\frac{\mathrm{F}}{a} = \frac{\mathrm{F}_0 - a + (\mathrm{F}_0 + a)\, e^{ax/\beta}}{\mathrm{F}_0 - a - (\mathrm{F}_0 + a)\, e^{ax/\beta}}, \text{ where } a = -4\pi\sigma.$$

The equation $8\pi\rho_0\beta + \mathrm{F}_0^2 = a^2$ gives $\mathrm{F}_0 - a = -8\pi\rho_0\beta/(\mathrm{F}_0 + a) = \rho_0\beta/\sigma$ very nearly, because F_0 and a must be nearly equal. Hence

$$-\mathrm{F}/4\pi\sigma = \left(1 - \frac{\rho_0\beta}{8\pi\sigma^2}\, e^{4\pi\sigma x/\beta}\right) \Big/ \left(1 + \frac{\rho_0\beta}{8\pi\sigma^2}\, e^{4\pi\sigma x/\beta}\right).$$

This gives

$$\mathrm{V} = -\int_0^t \mathrm{F}\, dx = -\beta \log\left(1 + \frac{4\pi\sigma^2}{\rho_0\beta}\, e^{-4\pi\sigma t/\beta} + \frac{\rho_0\beta}{16\pi\sigma^2}\, e^{+4\pi\sigma t/\beta}\right)$$
$$-\beta \log\left(1 + \frac{4\pi\sigma^2}{\rho_0\beta} + \frac{\rho_0\beta}{16\pi\sigma^2}\right).$$

In this expression

$$\frac{\rho_0\beta}{16\pi\sigma^2}\, e^{4\pi\sigma t/\beta}$$

is quite negligible for platinum, and $\rho_0\beta/16\pi\sigma^2$ is small compared with $4\pi\sigma^2/\rho_0\beta$, hence

$$\mathrm{V} = -\beta \log\left(1 + \frac{4\pi\sigma^2}{\rho_0\beta}\, e^{-4\pi\sigma t/\beta}\right) - \beta \log\left(1 + \frac{4\pi\sigma^2}{\rho_0\beta}\right).$$

This is almost the same as

$$\mathrm{V} = -\beta \log e^{-4\pi\sigma t/\beta} \left\{1 - \frac{\rho_0\beta}{4\pi\sigma^2}\right\}$$

or

$$\mathrm{V} = 4\pi\sigma t + \rho_0\beta^2/4\pi\sigma^2.$$

Let $4\pi\sigma t e = w$, and then

$$\mathrm{V}e = w + 4\pi\rho_0 e^3 t^2 \beta^2 w^{-2}.$$

Now $\mathrm{V}e$ is the work which an electron must do before it can escape, so that if N denotes the number of electrons in one gram-molecule, $\mathrm{R} = \mathrm{NV}e/\mathrm{J}$, where J is the mechanical equivalent of heat. Let $\beta = \beta_0\theta$, and we get

$$\mathrm{R} = \frac{\mathrm{N}w}{\mathrm{J}} + \frac{4\pi \mathrm{N}\rho_0 e^3 t^2 \beta_0^2 \theta^2}{\mathrm{J}w^2}.$$

If θ increases one degree, R therefore increases by $8\pi\mathrm{N}\rho_0 e^3 t^2 \beta_0^2 \theta/\mathrm{J}w^2$.

In the last section we got $\mathrm{R} = \mathrm{Q} + 2\theta \log (\mathrm{D}/\mathrm{A})$, according to which R increases uniformly with θ. But the experiments only extend over a small range of temperature, so that they are not sufficient to distinguish between the equations $\mathrm{R} = \mathrm{Q} + k\theta$ and $\mathrm{R} = \mathrm{Q} + k'\theta^2$, where k and k' are constants. The equation $\mathrm{R} = \mathrm{Q} + 2\theta \log (\mathrm{D}/\mathrm{A})$ depends on the assumption that Q, D, and A are all independent of the temperature.

The experiments show that Q and A do not vary much with the temperature, but it is quite possible that they really vary to some extent, for they cannot be found very exactly. Consequently I think it is justifiable to regard the two formulæ for R as equivalent over the range of temperature of the experiments, and so to put

$$2 \log (\mathrm{D}/\mathrm{A}) = 8\pi \mathrm{N} \rho_0 e^3 t^2 \beta_0^{\,2} \theta / \mathrm{J} w^2.$$

Now $\mathrm{N}w/\mathrm{J} = 4\pi\sigma te\mathrm{N}/\mathrm{J}$ is the value of R when $\theta = 0$, so it will be approximately equal to Q.

Hence we get $w = \mathrm{QJ}/\mathrm{N}$ and $\mathrm{Q}^2 \log (\mathrm{D}/\mathrm{A}) = 4\pi \mathrm{N}^3 e^3 \rho_0 t^2 \beta_0^{\,2} \theta / \mathrm{J}^3$.

If we suppose that the hydrogen in the layer consists of positively charged atoms, it will increase σ without altering t. If, then, a value of D can be found which will make $\mathrm{Q}^2 \log (\mathrm{D}/\mathrm{A})$ a constant, this may be taken to be the true value of D. Let $\mathrm{Q}^2 \log (\mathrm{D}/\mathrm{A}) = \mathrm{C}$, and then D and C can be found from two values of A and the corresponding values of Q. Taking the values

Q.	A.
145000	$1 \cdot 14 \times 10^8$
90000	5×10^4

gives $\mathrm{D} = 1 \cdot 44 \times 10^{10}$ and $\mathrm{C} = 10 \cdot 2 \times 10^{10}$. Using these values of C and D, we obtain the following values of $\mathrm{Q}^2 \log \mathrm{D}/\mathrm{A}$:—

Q.	A.	$\mathrm{Q}^2 \log \mathrm{D}/\mathrm{A}$.
145000	$1 \cdot 14 \times 10^8$	$10 \cdot 2 \times 10^{10}$
131000	$6 \cdot 9 \times 10^7$	$9 \cdot 0 \times 10^{10}$
110000	10^6	$11 \cdot 6 \times 10^{10}$
90000	5×10^4	$10 \cdot 2 \times 10^{10}$
56000	2×10^2	$5 \cdot 7 \times 10^{10}$

The five values of C agree as well as could be expected. We have, therefore,

$$10^{11} = 4\pi \mathrm{N}^3 e^3 \beta_0^{\,2} t^2 \rho_0 \theta / \mathrm{J}^3.$$

According to RICHARDSON's theory we have

$$\rho_0 = n_0 e = \mathrm{D} \times 3 \times 10^9 \, (\pi \mathrm{N} m/\mathrm{J})^{\frac{1}{2}},$$

where m is the mass of one electron. This gives, taking $e/m = -1 \cdot 8 \times 10^7$ in E.M. units and $\mathrm{N}e = -2 \cdot 9 \times 10^{14}$ in E.S. units, $\rho_0 = -2 \cdot 73 \times 10^{14}$ electrostatic units per cubic centimetre.

We have also $\beta_0 = 2{\cdot}8 \times 10^{-7}$, so that at $\theta = 1600$ we get

$$(4{\cdot}2 \times 10^7)^3 \times 10^{11} = 4\pi t^2 (2{\cdot}9 \times 10^{14})^3 (2{\cdot}8 \times 10^{-7})^2 \, 1600 \times 2{\cdot}73 \times 10^{14},$$

which gives $t = 2{\cdot}6 \times 10^{-8}$ centim.

The thickness of the double layer on platinum polarised by depositing hydrogen on it from dilute sulphuric acid has been calculated from the polarisation capacity by several observers who have found t about 2×10^{-8} centim. We should, of course, expect the thickness to be about of the order of the diameter of a molecule, which is believed to be about 2×10^{-8} centim. I think the fact that the theory proposed here leads to a value of t in agreement with that which might have been expected on other grounds shows that the theory is substantially correct.

Since platinum is an octovalent element we may take the number of free electrons associated with each atom as 8. The charge ρ_0 carried by the free electrons in one cubic centimetre of platinum ought therefore to be $8s\mathrm{N}e/\mathrm{M}$, where s denotes the density and M the atomic weight of the platinum. This gives

$$\rho_0 = -8 \times 21{\cdot}5 \times 2{\cdot}9 \times 10^{14} \div 195 = -2{\cdot}6 \times 10^{14},$$

which agrees very well with the value $-2{\cdot}7 \times 10^{14}$ obtained from the negative leak. The agreement between these two values of ρ_0 shows that all the 8 electrons associated with each atom of platinum are included in n_0, the number per cubic centimetre on which the negative leak depends.

Substituting the values found for D, A and Q in the formula $\mathrm{R} = \mathrm{Q} + 2\theta \log (\mathrm{D}/\mathrm{A})$, we get the following values of R :—

Gas.	Pressure.	R.
	millims.	
Air	—	$145000 + 9{\cdot}68\theta$
H_2	0·0013	$110000 + 19{\cdot}15\theta$
H_2	0·112	$90000 + 25{\cdot}14\theta$
H_2	133·0	$56000 + 36{\cdot}18\theta$

At $\theta = 2000$ these values are 164000, 148300, 140280 and 128360. The values of R at other pressures can be calculated, if desired, by means of the formula given in the last section.

A difficulty in the electron theory of the conductivity of metals has been pointed out by J. J. THOMSON in his book 'The Corpuscular Theory of Matter.' If the energy required to raise the temperature of the electrons one degree is calculated, it comes out greater than the specific heat of the metal. We have

$$p = -\beta\rho_0 = -\beta_0\rho_0\theta = \tfrac{1}{3} m n_0 \mathrm{U}^2,$$

where U^2 is the mean value of the square of the velocity of agitation of the electrons.

Thus $-\beta_0\rho_0\theta = \frac{2}{3}E$, where E is the kinetic energy of the electrons. Hence the energy required to raise the temperature of the electrons in 1 cub. centim. of platinum one degree is $dE/d\theta = -\frac{3}{2}\rho_0\beta_0 = \frac{3}{2} \times 2{\cdot}73 \times 10^{14} \times 2{\cdot}8 \times 10^{7}$ ergs. This gives $dE/d\theta = 2{\cdot}7$ calories, which is about three times the heat required to raise the temperature of 1 cub. centim. of platinum one degree at high temperatures.

It is possible that the number of free electrons per cubic centimetre is greater close to the surface of the platinum than inside. The value of ρ_0 deduced from the negative leak is, of course, the value close to the surface. Another very possible explanation of the difficulty is that D and ρ_0 have been over-estimated. If D is taken ten times smaller, or $1{\cdot}44 \times 10^{9}$, the energy required per cubic centimetre is only 0·27 calories per cubic centimetre, which is about one-third of the heat capacity per cubic centimetre. This value of D makes the thickness of the double layer 2×10^{-8} centim. instead of $2{\cdot}6 \times 10^{-8}$, and with it $Q^2 \log (D/A)$ is nearly as constant as with the value used. In fact, the possible error in D is at least a factor of 10, so that the difficulty about the specific heat is not very serious in the case of platinum if the value of ρ_0, deduced from the negative leak, is taken.

10. *Conclusion.*

The view taken in the above paper is that the effect of the hydrogen on the negative leak is due to its presence in the surface layer of the platinum. To explain this it is supposed that the hydrogen atoms are positively charged, so that they diminish the charge per unit area in the electrical double layer covering the surface of the platinum. The hydrogen appears to dissolve in the platinum at first, but at high pressures in time forms a stable combination, having a very small dissociation pressure. With new wires, before the stable compound has been formed, the leak is proportional to a power of the pressure of the hydrogen.

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[PLATES 9–25.]

REPORT ON THE ERUPTIONS OF THE SOUFRIÈRE IN ST. VINCENT IN 1902, AND ON A VISIT TO MONTAGNE PELÉE IN MARTINIQUE—PART II.

THE CHANGES IN THE DISTRICTS AND THE SUBSEQUENT HISTORY OF THE VOLCANOES

BY
TEMPEST ANDERSON, M.D., D.SC., F.G.S.

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VII. *Report on the Eruptions of the Soufrière in St. Vincent in* 1902, *and on a Visit to Montagne Pelée in Martinique.*

PART II.

The Changes in the Districts and the Subsequent History of the Volcanoes.

By TEMPEST ANDERSON, *M.D., D.Sc., F.G.S.*

Communicated by Professor T. G. BONNEY, *Sc.D., LL.D., F.R.S.*

Received January 11,—Read January 23, 1908.

[PLATES 9–25.]

IN 1902, Drs. ANDERSON and FLETT had the honour of being commissioned by the Royal Society to visit the volcanoes of the Soufrière of St. Vincent and Montagne Pelée in Martinique, and Part I. of their Report on the eruptions of the volcanoes was published in the Philosophical Transactions for 1903.*

It was intended that Part II. should include an account of the subsequent changes in the deposits of volcanic ejecta observed on that visit, and also on the petrology of the specimens collected in 1902.

In the Spring of 1907, Dr. ANDERSON revisited the West Indies, but Dr. FLETT being unavoidably detained in England by his official duties, Dr. ANDERSON is alone responsible for the field observations on the topography and geology, and also on the return of vegetation in the earlier portion of this Part II., while Dr. FLETT contributes the petrology. (See the following paper.)

By the kind permission of Sir DANIEL MORRIS, K.C.M.G., Mr. W. N. SANDS, of the Botanical Gardens, St. Vincent, was able to accompany Dr. ANDERSON to the Soufrière, and make a collection of the flora which is gradually reappearing on the devastated area. These plants have been identified by him, and also, where necessary, by

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* "Report on the Eruptions of the Soufrière in St. Vincent in 1902, and on a visit to Montagne Pelée in Martinique," Part I., by TEMPEST ANDERSON, M.D., B.Sc., F.G.S., and JOHN S. FLETT, M.A., D.Sc., F.R.S.E., 'Phil. Trans.,' A, vol. 200, pp. 353–553, Plates 21–39.

Sir Daniel Morris. Thanks are also due to His Honour E. J. Cameron, C.M.G., Administrator of St. Vincent, and to Duncan Macdonald, Esq., of Wallilabu, for their kind assistance and hospitality, also to the Rev. T. Huckerby, of Chateau Belair, for much help in visiting the Soufrière, and for information regarding the eruptions subsequent to the great outbreak of 1902. The author's special thanks are also due to Professor T. G. Bonney, F.R.S., and George Yeld, Editor of the "Alpine Journal," for much kind advice and literary assistance.

The map in Part I., Plate 39, shows that the north end of the Island of St. Vincent is formed by the cone of the Soufrière volcano. In the summit of this mountain lies the principal or old crater, nearly a mile in diameter, from which the eruption took place in 1902. There is likewise a much smaller crater, the so-called "new crater," which was active in 1812 and may have been formed in that year. These two craters are surrounded to the north by a large crater-ring of older date, broken down towards the south, which has been referred to as the Somma Ring, since it bears the same relation to the working cone of the Soufrière as Somma does to Vesuvius. The whole mountain group was formerly known as Morne Garu, but the name has now been appropriated to another mountain about three miles to the south, also formed of volcanic material, but of much older date, which is separated from the Soufrière by a deep depression extending right across the island. The part of this depression on the eastern or windward side of the island is occupied by the Rabaka and other smaller streams, and is called the Carib country, while that on the western or leeward side is drained by the Wallibu and other streams, and is here referred to as the Wallibu district. In the 1902 eruption a certain amount of the ejecta overtopped the Somma Ring and descended some of the valleys to the north of it, but by far the greater portion was discharged into the above-mentioned transverse depression. The water from the crater lake was discharged at the beginning of the eruption down the Rabaka and Wallibu Rivers, the former of which it rendered impassable, and thereby cut off escape from the Carib country, where the greater part of the deaths occurred, while the solid and gaseous ejecta in the form of the incandescent avalanches and black clouds* descended to both sides of the island, and the most important geological phenomena were observed in the Wallibu district. These phenomena, including the incandescent avalanche into the Wallibu valley, the partial re-excavation of that valley by the river, the secondary explosions of steam and hot ash, the discharges of boiling mud, and the formations of new fans at the mouths of the rivers, have been fully described in Part I., p. 428, *et seq.*; as has been also the subsidence of part of the coast between the mouths of the Wallibu and Morne Ronde Rivers (Part I., p. 453, *et seq.*). This district was therefore the part to which attention was specially directed in 1907, with a view of observing the further progress of these changes and the return of vegetation.

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* Called Nuée Ardente by the French Commission to Martinique, and later Nuée Péléenne. See Note, p. 298.

THE WALLIBU DISTRICT.

The Wallibu valley, like its fellow, the Rabaka, though profoundly modified by denudation, is not primarily a valley of erosion, but a gap left between the mountains of the Soufrière and Morne Garu as they have been built up stage by stage. The slopes of Morne Garu to the south are formed of old tuff and occasionally lava, all dipping away from the centre of that mountain and with their surfaces sloping towards the valley more or less conformably to the dip. This was very evident when the surface was bare of vegetation in 1902 (Part I., Plate 29, fig. 2). The north slopes of the Wallibu district, including in that term the area drained by the smaller parallel rivers of the Wallibu Dry River, Trespé River, Morne Ronde, and others, all to the north of the Wallibu, are composed of a series of beds of a newer date formed by ejecta from the Soufrière. They dip away from the crater of that mountain and abut unconformably against the older beds of Morne Garu. They have been dissected into flat-topped plateaux (Plates 9 and 14) by the above-mentioned rivers, which run in deep gorges with steep and often precipitous sides. These gorges have again been filled in places by ejecta of later eruptions, and re-excavated in different degrees and sometimes not along the old lines, leaving plateaux and terraces of different ages and heights. The lower valley of the Wallibu is a good example of this.* The river as it descends from the mountains in a westerly direction turns abruptly to the south, and then to the west again, after which it flows by a straight course of almost two miles direct into the sea.

The south or proper left bank of this lower portion was before the eruption of 1902, and is now again, moderately sloping and diversified by side gullies, almost deserving the name of valleys, in the old beds of Morne Garu, which show a fairly advanced stage of denudation. The north bank, on the other hand, is cut from a plateau, flat topped in the greater part of its extent, but with a rounded hill at its eastern end, and a moderate slope towards the sea on the west above the sites of the Richmond Estate House and Wallibu Works. Its top slopes gently to the south-west, and there is a terrace on the opposite bank of the river, near the lower end of the valley, which forms a continuation of the same slope, and shows that the plateau was once continuous across the valley which has since been excavated. Unlike the sloping bank opposite, it presents towards the valley a precipitous face in places nearly 200 feet in height. In the 1902 eruption this part of the valley was filled by the incandescent avalanche to a depth of at least 100 feet in the upper part, and to a smaller extent towards the sea, and it was in this deposit of hot ash that the steam explosions, slips of hot ash, flows of boiling mud, and other secondary phenomena took place. They are illustrated in Part I., Plate 29, fig. 2, where a deep channel is in progress of re-excavation on the south side of the valley, while a large plateau of hot ash still occupies its north side.

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* Part I., Map, Plate 39; Part II., Plates 9, 10, 11.

In 1907 almost the whole of this ash had been washed away, but a fragment remained in the shape of a terrace about 60 to 80 feet high, which showed the height to which the valley was originally filled (see Plate 10). It is situated on the north side of the valley, just below the abrupt turn to the west above mentioned, and is *in situ* except for a few partial landslides; the ash of which it is formed is unstratified and contains very few ejected blocks or fragments of any kind. The round hill behind it is the same as one shown to the left of the 1902 photograph in the middle distance. It was impossible to get a photograph from exactly the same position as before, since the ash bank on which the camera stood in 1902 has been all washed away, and the Wallibu plateau adjacent, when tried from several directions, proved inaccessible. The camera in 1907 was therefore placed on the floor of the valley in a similar position, but 60 to 80 feet lower. This floor, or more strictly terrace, as mentioned below, is all composed of water-sorted material, chiefly gravel and coarse sand, but with a good many blocks as big as a man's head. They represent ejected blocks and fragments of lava derived partly from the ash of 1902, and partly from older beds, the fine ash in each case having been washed away. The surface of the gravel bed showed marks of quite recent running water, and Mr. DUNCAN MACDONALD, who knows the place intimately, stated that during the last winter, 1906–07, the river ran along the foot of the north bank of the valley. When examined in March, 1907, it ran along the south side of the valley, and had already in those few months excavated a new channel about 30 feet in depth, as shown in Plate 11, which was taken from the top of the valley floor or terrace, the surface of which is shown in the previously mentioned Plate 9. The stratification as exposed in the side of this new valley is very distinct, and the sorting by water, mentioned above, is very evident. This gorge appears to have been excavated when the river was in flood, and as the water subsided and the excavating power became less, its channel in the bottom of the gorge became more tortuous, and it formed small meanders and left small terraces on its sides at different heights. This plate also shows the precipitous and inaccessible character of the north side of the valley where it is formed of the Wallibu plateau till it gets lower as it approaches the sea, and this is a characteristic specimen of the early stages of denudation in these ash beds.

The south side, on the contrary, is sloping, and its outline is characteristic of a more mature stage of denudation. This sloping character has enabled more numerous terraces of the new deposits to survive. Some low down by the side of the river consist solely of water-sorted material, while others show patches of ash in its original condition higher up the slope. In one or two cases it is possible to compare the two in juxtaposition (Plate 12, fig. 1), in which case the lower terrace of water-sorted material stands almost vertical where it has been undermined by the river in two stages; while behind it a mass of ash *in situ* shows most beautifully the marks of rain-water running over and down the surface. Further away again, the slopes of the old valley show denudation in a more mature stage.

Further up the mountain the remains of the avalanche became more abundant in the valley bottoms (Plate 13), and here they were also often better preserved, so that traces of the feather-pattern erosion, so noticeable in 1902,[*] were still visible on the surface. This was mainly due to the surface of these ash deposits, like those to be presently mentioned on the plateaux and on the ridges, having consolidated into a crust almost like a cement pavement which resists the action of the rain. Another very curious and, it is believed, novel point was observed with regard to these massive ash deposits. Instead of one stream re-establishing itself along the centre of the deposit, the tendency is for a new stream to form on each side at or near the junction of the new ash with the old valley walls, and as these streams deepen themselves, two new valleys are formed where only one previously existed, and the walls of each are composed on the one side of the new ash, and on the other of older tuff with occasional terraces of new ash. Sometimes the two valleys coalesce by the washing away of the central mass, but quite often the two remain distinct, as in the case of the Trespé River[†] and Wallibu Dry River to be mentioned shortly. The fact of this side formation of streams is clear; it is seen in the ravine just noticed, also in the upper Rozeau, and in several of the plates in Part 1, where, though not noticed at the time owing to its being then in an early stage, it is distinctly visible when looked for, but the cause is not so clear. It appears to be due to the fact that the water from the old slopes in running down into the original valley meets the soft new ash, and at once turns down along the valley and so starts the new stream, and it seems likely that the chief cause of its so turning is that the surface of the deposit tends to be higher along the middle of the valley than at the sides, the shape of the mass somewhat resembling a glacier, which it is well known is usually higher in the middle because of the more rapid motion of that part.

The Wallibu Dry River and Trespé River.—These are two small and short rivers to the north of and parallel with the lower part of the Wallibu valley, and both run in deep gorges in the floor of a wide valley bounded on the south by the Wallibu plateau. In 1902 both these gorges were filled with new ash to the level of the main valley floor, and the process of re-excavation of one of them is shown in Part I., Plate 30, fig. 2. It was noticed that this main valley was wider and more open than the Wallibu valley,[‡] but no explanation was forthcoming at the time. Mr. DUNCAN MACDONALD now informs me that before the 1812 eruption the Wallibu River flowed down the Wallibu Dry River, and that its course was changed after that eruption. Mention has already been made of the Wallibu valley making an abrupt turn to the south and turning again to the west round the

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[*] Part I., Plate 26 and Plate 28, fig. 1.

[†] I heard this river called also Cobrée. The confusion is due to these gorges being liable to be filled up and re-excavated in slightly different positions.

[‡] Part I., p. 429.

end of the Wallibu plateau. The line of this upper part of the valley, if prolonged to the sea, passes to the north of the Wallibu plateau down the broad valley of the Wallibu Dry and Trespé Rivers, and is blocked opposite the east end of that plateau by a great deposit of ash, which has deflected the river into its present course (Plate 9). Below this obstruction the broad open valley can still be traced as described above, while its floor is now occupied by the two small river valleys above mentioned, divided by a plateau or ridge often only a few yards wide, and sometimes a mere knife edge. It is formed of ash different from and less consolidated than that composing the walls of the main valley, and its top is considerably lower than the Wallibu plateau. A closer inspection of the Trespé valley (Plate 12, fig. 2), where the narrow gorge has been emptied of the 1902 ash, now shows that the north wall is much higher than the south, and also formed of older and more consolidated tuff. If the sides of the picture were reversed, it might serve as a view in the Wallibu Dry River, the higher bank being in this case the Wallibu plateau to the south. It is thus clear that these two rivers are an example in a more advanced stage of the process which, as described, is now taking place in the ash of 1902 in the ravine above mentioned.

The Wallibu plateau is composed of ash older than that dividing the above two small rivers, but still comparatively new, and its flat top and precipitous sides, both north and south, proclaim it to be in an early stage of denudation, while the south bank of the Wallibu is composed of older tuff and lava, and shows a much more mature type of denudation, viz., sloping hills with rounded or ridged tops, and a good deal weathered into valleys or gullies. The same description would apply to the north face of the plateau, which is precipitous and obviously much less advanced in weathering than the slopes of the Soufrière on the opposite side of the valley to the north. The mass appears to be the remains of an avalanche or succession of avalanches of hot ash poured into the depression between the Soufrière and Morne Garu, on an enormously bigger scale than anything formed by recent eruptions. It would seem that the present bed of the Wallibu to the south, and the broad valley of the Wallibu Dry and Trespé Rivers to the north, are each the enlarged and deeply excavated development of the valleys that were formed at the sides of this prehistoric avalanche.

The Fans and Low Plateaux.—The part of the Wallibu district between the sea and the Wallibu plateau, and others like it, of comparatively old date, consist of a series of low plateaux and fans (Plate 14). These have been formed by a succession of discharges from the Soufrière, which are mostly unstratified, and have been partly or wholly consolidated into tuffs. They are much dissected by ravines cut by the rivers, and the materials brought down by these have formed fans and deltas consisting of water-sorted materials. Sometimes the rivers in the earlier stages of their cutting through the plateaux have deposited water-sorted beds on their surfaces, which are interbedded with those of ash *in situ*, rendering the structure more complex, while the fans laid down in the earlier stages of denudation after an eruption are dissected by the rivers later on, leaving terraces at one or both sides which merge into the plateaux. The plateaux and fans thus pass insensibly one into another, but on the whole it will be convenient in this paper to restrict the term "fan" to the portion over which the river at present habitually flows at intervals, and reserve the term "plateau" for the more completed and generally higher portion over which such a flow no longer generally occurs.

In the eruption of 1902 the incandescent avalanche which came down the Wallibu, as soon as it had passed the deep part of the valley, spread like a fan over the plateaux to the north and south. To the south it turned round the lower end of the Richmond ridge, where it formed, along with water-borne material, a bar at the mouth of the Richmond River. This bar still exists, though much washed away. The river has cut a sinuous channel through it. The shore of the plateau, which in 1902 was sloping,* is now washed away into a steep cliff 30 or 40 feet high. There is only a narrow steep beach at its foot. The plateau at a little distance from the shore is about 50 feet in height, and the older portion further inland about 150 feet, or three times as much.

The fan of the Wallibu in 1902 extended beyond the coast line, and was very steep. Gushes of hot mud came down it,† and tended continually to build it up. In 1907 it scarcely extended beyond the coast line, and both have receded considerably. The fan is no longer steep, but has only a very gentle slope, as shown in Plate 14, which is taken from the plateau just mentioned. The river appears to wander frequently about this fan, as it does further up the valley. In March, 1907, it flowed at the south side of the fan, close under the above-mentioned cliff, and is consequently concealed behind it in the photograph. The avalanche, where it spread north towards the Richmond Estate House below the end of the Wallibu plateau, was of unequal thickness. This, in a good section on the north bank of the Wallibu fan, was from 10 to 20 feet, and, curiously, it was greater nearer the sea coast. The section exposed extended in places to below the old surface, and the line was marked by the vegetation which was returning in the old soil.

The plateaux to the north present similar features in the re-excavated river valleys. They show good sections of soft tuff, with a capping of new ash, generally from 10 to 20, or even more, feet in thickness, and the line of the old surface is here again visible by the return of vegetation. Except about the Wallibu House and Works, their surface is generally bare and consolidated into a crust.

The Wallibu Subsidence.—This took place along the shore north of the Wallibu and south of Larikai Point. The foreshore to a breadth of about 200 yards and a length of above a mile appears to have subsided into deep water by a sort of submarine landslide, a secondary effect of the earthquakes connected with the eruption.

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* Part I., Plate 24, fig. 1.

† Part I., Plate 23, fig. 2.

Further slides are reported to have taken place at the times of the eruptions in September, 1902, and March, 1903, but this is not very certain. The cliffs in this part are higher than further south, but present similar structural features, viz. :—tuff capped with new ash (Plate 14). A new beach is forming along the base, the materials of which appear to be furnished partly from the cliffs, partly by that brought down by the rivers. The gorges cut through this plateau are often very narrow, and their steep sides show fine sections of the tuffs and ash beds.*

THE SOUFRIÈRE.

The Upper Slopes.—The upper slopes of the mountain are chiefly formed of beds of tuff like the lower parts, but contain perhaps a larger proportion of ejected blocks which naturally fell in greater abundance nearer the crater. They are much cut up into deep ravines which are separated by the ridges, the slopes of which are often very steep, as described in Part I.† Even in 1902 the new ash, which had never been thick on these slopes, was in great part washed away, and it was only on the ridges and in some of the valley bottoms that any considerable amount of that ash remained, and this process, of course, has gone on ever since.

The ash on the ridges still remains, and its surface is consolidated into a thin but hard crust similar to that on the plateaux. This extends generally only to a width of a few feet, and often not more than one or two. On each side of the ridge where the ash has been washed away the old soil has been exposed, and it would doubtless also have been in a great measure removed if it had not been held together by the roots of plants which, as mentioned below, were in many cases not killed. Even when dead they no doubt held the soil together to a large extent while the new vegetation has been re-establishing itself.

The old Carib track to the summit ran along one of these ridges (Plate 22, fig. 2), and the consolidated ash forms in most parts an excellent footpath along the former lines. It is true that in places the ridge has been carried away by landslides, but a comparatively small amount of labour would suffice to restore it to a perfectly useful condition. The path for a considerable distance overlooks the upper part of the Rozeau valley, which extends nearly to the summit of the mountain, and this is a good example of a high valley in which extensive ash deposits were formed. It was here that Mr. T. M. MACDONALD saw explosions in the earlier stages of the eruption, and these were supposed to proceed from parasitic craters, *i.e.*, side branches of the main chimney. The place was pointed out to me by his brother in 1907. It was impossible to approach it closely except at unjustifiable risk, but an examination from a distance of perhaps 100 yards revealed nothing but a hollow in a bed of ashes, which no doubt was merely the locality of a secondary explosion in the hot ash like those

* Plate 12, fig. 2. In lower Trespé valley.

† Part I., Plate 31, fig. 2, and Plate 35.

described in Part I., p. 438. This body of ash, which is well seen from near the Maroon tree about half way up the mountain, presents one of the best examples of the rounded character of the deposit in its original state, where, as mentioned above, it was higher in the middle than at the edges.

The Crater.—In 1902 we ascended to the lip of the crater twice, from the south-west and south-east sides respectively, by the old Carib track which led from Chateau Belair, *viâ* Wallibu, on the leeward side to lot 14 and Georgetown on the windward side of the Island, but owing to the summit being in cloud on each occasion we saw only rare glimpses of the interior. In 1907 I was more fortunate, and during part of the time I was on the summit the air was perfectly clear, though the clouds came down before I had an opportunity of examining the new crater. The topography of the old crater is still correctly represented on the Admiralty chart. The crater is approximately circular, nearly a mile in diameter at the rim, and with a lake in its bottom (see Plate 15).

The walls in the greater part of their height are nearly vertical, and consist of alternate layers of tuff and compact rock, all dipping outwards from the crater. The latter beds are chiefly lenticular in section and columnar or subcolumnar in structure, the columns being as usual arranged at right angles to the surfaces of cooling. Probably they are chiefly lava flows, but some may be intrusive sheets. It was impossible to get near enough to examine their surfaces of contact with adjacent beds. There is a very prominent dyke to the north-west of the crater and a smaller one to the west of it, which cut through several of the massive beds referred to, so that, as intrusive action has undoubtedly occurred, the results might be horizontal sheets as well as vertical dykes. One of the horizontal beds mentioned above, situated in the north-west wall of the crater, is especially massive. It must be several hundred feet thick and is distinctly columnar. At the foot of the almost vertical cliff is a broad bench or beach, specially well marked on the north and east side of the crater. The Rev. T. HUCKERBY, of Chateau Belair, who has ascended the mountain many times, is quite clear that it was formed by the ejecta of the small eruption of March, 1903. It has suffered much erosion by rain and other agents of subaerial erosion, and a talus is forming on it in places by falls from the cliffs above.

The topography of the crater lake also corresponds with that marked on the Admiralty chart, and the sheet of water appears to be a trifle over half a mile in diameter. Mr. HUCKERBY thinks it is at a somewhat lower level than before the eruption, but Professor KARL SAPPER'S measurements render this doubtful.* The water is of an uniform light green colour and does not boil or steam in any part. The mottled appearance in Plate 15 is due to reflections from the clouds. The lake is not in any way divided, and no secondary cone is visible. If any exists it must be below the water level. There is one spot near the foot of the crater wall on the south side where vapour escapes occasionally in small quantity, and

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* See p. 291.

another still less evident on the east. Neither is sufficiently conspicuous to appear on the photographs. Thus all the deeper parts of the crater bear evidence of the severity of the eruption of 1902, since it appears that any loose deposits previously existing there have been entirely blown out, and that the small bench or talus mentioned above is of subsequent formation. The upper parts of the walls of the crater are on the whole less precipitous than those lower down, and are in places, especially on the south and south-west, covered with a deposit of new ash apparently only a few feet thick (Plates 16 and 18). It dips towards the crater at the angle of repose between 30° and 40° and has been much denuded by the rain. There are only a few places, however, where it is sufficiently continuous to obscure the solid beds, and where these are visible ash and tuff predominate over lava, the reverse of which is the case lower down. On the north the wall is considerably higher than on the south, and the precipitous portion extends higher up. The beds of tuff, which are here particularly well developed, contain many large ejected blocks (Plate 17). This abundance of ejected blocks to the north-east of the crater agrees with the observation of Mr. T. M. Macdonald during the eruption of 1902, that most of the stones thrown out went to windward, so that the direction appears to have remained unchanged from an earlier period. The figure to the right is standing on a lower portion of the rim (Gap A in several plates) near the point where the Carib track begins to descend in a south-easterly direction to the windward side of the island, and through this gap, no doubt, the black cloud and avalanche descended which devastated the Carib country.

This lip of the crater is usually quite narrow, generally only a few feet, occasionally a few yards, wide, as shown in Plate 16. It is mostly composed of a bed of new ashes a few feet thick, almost everywhere consolidated on the surface into a crust, generally less than an inch thick, as in the case of the ridges lower down. Where this crust is entire it has preserved the rest of the bed from erosion, but whenever it has been broken through, the whole of the deposit has generally been washed away, and this is particularly noticeable on the outer slopes, where the beds of new ash lie conformably on the old ones and weather off in successive layers. The lip is by no means regular or uniform in height. It is highest to the north. Besides the gap just mentioned (Gap A), it presents three well-marked gaps, B, C, and D, of which B is shown in Plate 16, and D, the more westerly, in greater detail in Plate 18. B and C are on the south of the crater; of these the more westerly, C, is somewhat the lower, and both are lower than A. It was doubtless through them, and presumably through the lower one especially, that the water of the crater lake and the incandescent avalanche descended into the Wallibu and Rabaka districts.

The other gap, D, Plate 18, occurs more to the west, where the lip of the crater joined the Somma ridge; as the whole of this part of the rim of the crater is much higher than the southern portion, the bottom of the gap, deep as it is, still remains higher than B and C. This gap, D, leads down in the direction of Larikai and Morne Ronde. It was lowered considerably during the eruptions of the autumn of 1902, and this accounts for the greater deposits in the Larikai valley in the later eruptions. The Somma Ring (Plate 18) is seen to consist of beds of lava and tuff dipping outwards from the crater, conformably with the outer slope of the mountain. The whole of the interior of the crater is still quite bare and without any trace of returning vegetation. A few small patches of moss appear on and about the rim, and in somewhat greater abundance on the slopes outside. This is worth notice, for Mr. JAMES ANDERSON, in 1784 (Part I., p. 461), found moss covering the inside of the crater and in great abundance on the cone at the confines of the grassy region and the barren, so that the conditions are presumably becoming similar to those which existed at that time, and the vegetation will eventually be as it was before the eruption of 1902.

The Carib country was not visited*, but as far as could be judged from a distant view from near the top of the Soufrière, vegetation was returning in a manner similar to that in the Wallibu district, and Mr. SANDS, who has since visited the district, assures me that this is the case. He states that there is water in the upper reaches of the Rabaka River, though it all sinks into the ground lower down, so that none reaches the sea. The old bed of the river has become blocked about a mile from the sea and a new course has been formed to the north of it. The restoration of the water supply to the district, by the repair of the old conduit, is under consideration.

The difference between the character of the eruptions of the Soufrière and Montagne Pelée, mentioned in Part I., p. 533, appears to have continued since 1902, the outbursts from the former volcano being generally less frequent but more violent than those from the latter.

THE RETURN OF VEGETATION.

Confining our attention for the present to the Wallibu district, it may be stated generally that the whole of the country north of Morne Garu was devastated in different degrees. The limit of the zone of devastation extended right up to the summit of Morne Garu, and the line followed the main ridge in a westerly direction almost to the sea, before reaching which it diverged so that the Richmond Plantation Works were included, but the south bank of the river was not materially injured (Plate 19). Within this area the bottoms of the valleys, which were covered by the incandescent avalanche, had their vegetation utterly destroyed. In other places, where the hot ash was only deposited in a thin layer, the roots were in many cases not killed outright and are now throwing up new shoots and leaves, though the large trees are almost universally killed, except in a few sheltered situations.

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* Arrangements had been made to return by what was then advertised as the last voyage of the Intercolonial Service of the Royal Mail Company.

The localities may now be discussed more in detail. The conditions at the Richmond Plantation Works may be taken as a type of those of all the low ground near the limit of devastation. The incandescent avalanche swept down the Wallibu valley and spread out over the old fan or plateau at its mouth, it then turned south round the lower end of the Richmond ridge and destroyed the Richmond Works and all the vegetation near them. The ash still remains to a depth of two to six feet in different parts, and the old roots are completely buried and thoroughly destroyed, but the avalanche was confined to the bottom of the valley, and none of its effects are visible on either side. The black cloud which accompanied the avalanche either did not keep to the ground beyond the ridge behind the Works or had lost most of its heat, and on this slope there are Gru Gru palms (*Acrocomia sclerocarpa*), which though injured are recovering, and one silk cotton tree (*Eriodendron anfractuosum*) at the Works is still alive (Plate 19). In other places, however, further to the east, some trees are killed, but this appears to be the limit of devastation. The surface of the ash near the Works has not consolidated, but is rapidly breaking up under the influence of plant roots, and humus is being formed. The chief new plants are Castor Oil (*Ricinus communis*), which grows in luxuriant masses along and around the ruins of the Works, and a plant, Cattle Tongue (*Pluchea odorata*), which has already formed flourishing bushes taller than a man (Plate 20, fig. 1). Besides these, Indigo (*Indigofera Anil*), Sensitive Plant (*Mimosa pudica*), Guinea Grass (*Panicum maximum*), *Eupatorium odoratum*, and two grasses (unnamed) were also noticed. On the hill sides, grasses and a few trees, such as Gru Gru palm (*Acrocomia sclerocarpa*) above mentioned, Walnut (*Andira inermis*), Fiddle Wood Tree, and *Ficus* sp. Near the river the Rozeau Grass (*Gyncrium saccharoides*) is also growing luxuriantly to a height of 12 or 15 feet (Plate 20, fig. 2).

At the foot of the seaward slope of the Richmond ridge is a fan, or plateau, which was covered several feet thick with the incandescent avalanche, the end of which is mentioned above as extending up the valley as far as the Richmond Works (Plate 21). Here the surface has consolidated into a crust nearly an inch thick, almost like a concrete pavement, and where this crust is perfect no vegetation can spring up; where, however, it is broken up, as along the small water courses, Silver Ferns (*Gymnogramme calomelanos*), grasses and young Plucheas are getting hold and their roots are spreading into the harder parts on each side. In places also the crust is being broken up by the trampling of horses and cattle, and the process of return of vegetation is thereby being hastened. The lower end of Richmond ridge above this fan was only slightly affected.

Further to the north along the coast there are several other plateaux on which the vegetation is making similar progress (Plate 14). They are much cut up by ravines, in the precipitous walls of which, and in the sea cliffs, the old soil is generally exposed at a junction of the old tuff and new ash above it, and this line is often marked by a band of luxuriant growth from the old roots. The Wallibu Plantation (Part 1, Plate 25, fig. 2) was situated on one of these plateaux below the end of the main Wallibu plateau. The vegetation is here more advanced than on the surrounding flats, and it had almost concealed the aqueduct, which is such a conspicuous object in the 1902 plate; Bamboo (*Bambusa vulgaris*) is growing luxuriantly and the other plants are practically the same, and their growth is about as much advanced, as at the Richmond Plantation.

In the Wallibu valley vegetation has made little progress, the floor being composed of ash and gravel which is still liable to re-arrangement by every flood, but on the south slopes leading up to the Morne Garu range the return has been considerable. The surface is still studded with the charred and bleached skeletons of trees, which appear to have been killed universally, with the single exception of a small lateral valley north of the lower part of the Richmond ridge, where a few palm trees in a sheltered position have recovered. The shrubs and herbaceous vegetation, which were all burnt level with the ground, are gradually returning, in many cases from the old roots, since the removal of the thin covering of ashes by the rain. The north wall of the Wallibu valley is precipitous and only recently relieved of its covering formed by the incandescent avalanche, and is still almost bare of vegetation. The top of the Wallibu plateau was entirely devastated. The trees remain only as bleached trunks except a few which have recovered in sheltered positions at the ends and south edge of the plateau (Plates 9, 10, 11). The dead trunks show that the ash was never more than a few feet thick at the most, and the whole is now covered with a luxuriant growth chiefly from the old roots.

In the smaller gorges to the north, such as the Wallibu Dry River and Trespé discussed above, vegetation is making more progress than in the Wallibu. Their precipitous sides are becoming densely covered with Silver Ferns (*Gymnogramme calomelanos*) and creepers such as Ipomœas, besides grasses and herbaceous plants (Plate 22, fig. 1).

Along the slopes of the Soufrière, of which the ridge followed by the old Carib track may be taken as an example, the return of vegetation is very marked. All the trees without exception are killed and their stumps are becoming covered with Ipomœas and other creepers, while, the ash having been much washed away, except along the ridges, the old soil is mostly exposed (Plate 22, fig. 2) and the vegetation is returning chiefly from the old roots and their progeny. In the lower part, as for instance where the track rises steeply out of the Trespé valley, the vegetation is so luxuriant as to form a tropical jungle dense enough in places to require the use of a cutlass to effect a passage through it (Plate 23, fig. 1). At about this height are masses of Rozeau (*Gynerium saccharoides*), *Heliconia Bihai*, Tree Fern (*Cyathea arborea*), a few trees, and a large number of shrubs and herbaceous plants, grasses and creepers (Ipomœas chiefly), and the same flora continues up to the Maroon Tree, which is at a height of about 1000 feet.

At about 800 feet Tree Ferns (*Cyathea arborea*) become very abundant and large sheets of them are common (Plate 23, fig. 2), and generally it may be said that vegetation is luxuriant up to a height of about 1000 feet, abundant up to 1500, and very sparse above that height, with only a few grasses and silver ferns; higher up nothing but mosses and lichens are found.

At the lower lip of the crater and just inside it mosses and lichens only are found. The mosses have been identified at Kew as: *Pogonatum tortile*, P. BEAUV., and *Philonotis tenella*, JAEG., and the lichen as *Stereocaulon* sp.

On the higher slopes of the Carib country vegetation is much the same as on the leeward slopes at about the same elevation.

The coast north of Morne Ronde and Larikai Point was only examined from a canoe, but on this side of the mountain vegetation appeared to be returning in a manner similar to that on the more accessible parts. Most of the plants were the same as at Richmond and Wallibu, and the Trumpet Tree (*Cecropia peltata*) and Bois Flot (*Ochroma lagopus*) were also noticed.*

THE HISTORY OF ERUPTIONS AFTER MAY, 1902.

The Eruption of September 3 *and* 4, 1902.—Through the courtesy of His Honour C. J. CAMERON, Administrator of St. Vincent, and Sir DANIEL MORRIS, of the Imperial Agricultural Department, and other officials, I have been allowed access to reports by Mr. POWELL, of the Botanical Gardens, St. Vincent; Professor RADCLIFFE HALL, Professor LONGFIELD SMITH, and Mr. ALLAN, the Revenue Officer of Chateau Belair. The Rev. T. HUCKERBY, of Chateau Belair, Mr. MACDONALD, and the Rev. JAS. DARRELL have also furnished notes. From these sources the following account is condensed.

After the eruptions of May, 1902, the crater remained quiescent, but earthquakes were noticed at the Botanical Gardens on July 17th and 21st, and by the Rev. T. HUCKERBY at Chateau Belair on the 9th, 19th, 20th, 23rd, 30th, and 31st of the same month. The shock of the 17th occurred at 9.45 a.m., as noted by Mr. POWELL, and was preceded by a noise rather like a bomb exploding. The movement was up and down, and the duration about six or eight seconds; that of the 21st took place at 1.10 a.m. The movement was from north to south, and the duration also six or eight seconds.†

A party who visited the Soufrière on the 12th of August saw small openings (fumaroles) on the lip of the crater from which steam and small pebbles escaped.‡

On September 3, from 6 a.m., a series of explosions commenced, which increased in violence as the day wore on, and at 9 p.m. the detonations became very loud. The

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* The return of vegetation on Krakatoa presents many points of similarity. 'Treub. Annal. Jard. Botan. Beutenjorg,' 7, 1887–8.

† Mr. POWELL'S Report, September 12, 1902.

‡ 'Sentry,' August —, 1902.—Some of the newspaper cuttings do not retain the date of issue.

eruption reached its climax about 2 o'clock in the morning of the 4th. A black cloud alive with electric displays stretched itself from the north to the south of the island; at 3 a.m. the detonations had become less regular, and at 3.55 a.m. an earthquake was noticed at Chateau Belair, and also at the Botanical Gardens, where the explosions were considered louder than in May, the "din" being described as terrific. From this time the eruptions became less violent, though slight rumblings continued throughout the day till 5.30 p.m. It was noticed during the eruption that material like mud flowed from the crater down the Larikai valley. There was a heavy fall of ash on the leeward side of the island. Beginning as a thin layer at Barualli, it gradually increased to five to nine inches at Chateau Belair, where several buildings were injured by the heavy fall, which consisted of dust, lapilli, and black stones. Very little ash fell at Georgetown, or the windward side, and the mountains in the middle of the island showed no change in appearance. Mr. POWELL made an official visit to some native allotments on the leeward side of the island, about four miles south of the volcano, in order to estimate the damage. At Rosebank, on the seashore, the thickness of the deposit was about three inches. It consisted of coarse ash and pieces of pumice stone up to three inches in diameter, with solid stones of the size of gravel and occasionally larger. For 1¼ miles inland the damage to the native provision grounds was very great, but for the next mile much less. No lives were lost.*

On Sunday, September 21, there was a sharp, but short explosion, very striking in appearance. The people were much frightened, and asserted that there was a greater accompaniment of "fire" than on previous occasions. Part of the red glow, however, may be attributed to the setting sun.†

On September 18 the telegraph cable to the north, which had been repaired only the previous day, was again interrupted.

On Friday, September 22, Mr. HUCKERBY‡ made an ascent of the Soufrière. For some distance, whilst crossing the Wallibu valley, he had to walk ankle deep in mud. On the lower ridges he found a plentiful supply of fine ash. About 400 feet below the summit a large number of newly ejected blocks were lying about in all directions. Great changes had taken place within the crater. He estimated it to be 150 feet deeper than it was immediately after the eruption of the 7th of May. A considerable amount of ash was banked up against the northern wall and part of the eastern side, which had become almost perpendicular, while a large portion of the Larikai (W.) side had been blown away and the lip lowered several feet. A fissure had been formed on the southern lip, from which steam was slowly ascending. The bottom of the crater contained a small lake of stone-coloured liquid, which was constantly boiling up and sending forth clouds of steam.

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* Mr. POWELL'S Report, September 12, 1902.

† Letter from Mr. MACDONALD, of Wallilabu.

‡ Rev. T. HUCKERBY, in a letter to Dr. ANDERSON.

Mr. Huckerby noticed after the eruption that further subsidences had taken place north of the mouth of the Wallibu River, as had happened in the May eruption.

The Eruption of October 13 *and* 14, 1902.—This appears to have been the most severe eruption since May, 1902. Mr. Huckerby writes[*] :—"On the 1st and 13th of October there were electric displays over the crater, and on the night of the 12th a lunar halo was observed. The 13th and 14th were days of intense heat, and several earthquakes were felt at the northern end of the island. At about 8 p.m. on October 14, slight rumblings were heard, and clouds of dust-laden steam were ejected from the crater, but everything passed off very quickly. At midnight the activity recommenced and violent detonations disturbed the people of the district. At 12.30 a.m., what appeared to be a ball of fire presented itself over the crater, followed by a flow of red-hot matter down the Larikai side of the mountain. At the same time a mist-like circle appeared over Chateau Belair. At five minutes to two, stones began to fall in Chateau Belair and continued for about two hours. The electrical displays were terrible to behold, and the thunder cannonaded with a deafening roar. Mud began to fall at 2 o'clock. I noticed four earthquake shocks, the two at 3.22 a.m. and 4 a.m., respectively, being the heaviest and most prolonged. The detonations became irregular between 4 and 5 o'clock and died away gradually. At 8 o'clock in the morning the crater was sending forth volumes of dust-laden vapour, which action continued until the 17th. Stones, some probably two pounds in weight, were picked up at Chateau Belair on the morning of the 15th. Most of the ejecta were carried out E. and N.E. of the island. The Carib country was covered with large stones and coarse material."

The débris fell chiefly upon the windward side of the island. The Carib country, as it had been previously utterly devastated, did not attract much attention, but Mr. Powell[†] visited the still inhabited districts and noted the amount of damage. At Kingston there was from $\frac{1}{8}$ to $\frac{1}{4}$ inch of ash. Further north it gradually increased in thickness. At Gregs and Union Estates 2 inches were measured, and at Park Hill 3 to 4 inches, while at Georgetown and Mount Bentinck the depth was 6 to 8 inches. Much damage was done to the provision grounds of the natives in all the localities, which the newspapers describe as utterly ruined. The ash was very hot, but apparently from the heat of the sun. The dust was carried as far as Barbados, where detonations were heard, and samples were collected at the Government Laboratory, and also by the U.S. Weather Bureau, and the Rev. N. B. Watson, St. Philips. Professor Radcliffe Hall gives the amount collected at the Laboratory as follows :—

	Tons per acre.
October 16, from 9 a.m. to 11 a.m., at the rate of	0·48
11 a.m. to 1 p.m. „	2·10
1 p.m. to 3 p.m. „	1·34
Total from 9 a.m. to 3 p.m. „	3·92

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[*] In a letter to Dr. Anderson.

[†] Powell, Report of October 24, 1902.

He also collected samples at Rosebank and Hastings, where the amount from 8.45 a.m. to 4 p.m. on October 16 was 4·49 tons per acre.*

Mr. POWELL and a party ascended the mountain on October 28, 1902, and found that the old crater was discharging volumes of steam and that numerous cones of ashes were being thrown up to a height of 30 or 40 feet from a fissure close under the southern wall.† The lake was boiling near the centre. The steam as it rose was carried along the south-eastern wall to the eastern edge of the crater, where it became visible to observers in the low country and created the erroneous impression that the new crater was in eruption.

On Wednesday, November 26, 1902,‡ there was a considerable flow of mud down the Rabaka River. The ash avalanches of the May eruptions had completely blocked its bed, and the ejecta of the subsequent eruptions had doubtless contributed their quota. As a result there was no water in the channel, and this in spite of the heavy rainfall of five months. On November 26 the stream at last got vent, and two raging, steaming torrents descended the valley. One of these destroyed the remains of the Rabaka Sugar Works, and for the last mile before reaching the sea the old course has been blocked up and the river now runs in a new channel to the north of the old one. It is supposed that a lake had formed in the higher reaches of the river which at last had got vent, but details are wanting.

Mr. HUCKERBY writes§: "Detonations were heard on the 19th and 22nd of October and on the 6th, 11th, and 24th of November, 1902. On the 26th of November there was a minor eruption and a small quantity of ash and lapilli fell at Georgetown and Chateau Belair. On the 22nd of January, 1903, at 12 noon, there was again a minor eruption with a projection of very dark steam and a little ash. Detonations were heard on the 22nd, 24th, 26th, and 28th of January and on the 6th of February. Steam was emitted from the crater on the 13th, 14th, and 28th of February."

Professor SAPPER, of Tübingen,‖ ascended the Soufrière on February 6, 1903, with the Rev. T. HUCKERBY, of Chateau Belair, and paid a visit to both the new and the old craters, this apparently being the first to the new one since the eruption. They found that owing to landslides into the crater the gap above the Larikai valley was deepened. They had considerable difficulty in crossing it, and in order to do this had to descend some distance. Dr. SAPPER made a plan of the crater and found that no material alteration had taken place in its shape from that indicated on the English Admiralty Chart. The diameter in every direction was about 1320 metres (4331 feet),

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* 'The Agricultural Reporter,' October 20, 1902.

† 'Sentry,' October 31, 1902.

‡ 'Barbados Advocate,' December 3, 1902.

§ In a letter to Dr. ANDERSON.

‖ "Der Krater der Soufrière von St. Vincent," von KARL SAPPER, 'Centralblatt für Mineralogie,' Stuttgart, 1903, pp. 369–373.

but the north wall being higher than the south the plane of measurement was inclined in that direction, so that on a level the shape was really somewhat oval, with the long diameter from the W.N.W. to E.S.E. The lake was also oval, with its diameter in the corresponding direction. Its length on February 6 was 540 metres (1772 feet), its breadth 340 metres (1116 feet), and the height above the sea-level 585 metres (1919 feet),* which agreed almost exactly with that given on the chart (1930 feet). The water was boiling in the centre and also at the south-east corner. The district between the Somma wall and the two craters was deeply covered with ejecta. The new crater was filled up almost flat. It had a small shallow lake (about 70 metres (230 feet) in diameter) towards its eastern side, with water marks which showed that it had been bigger. The saddle, which previously separated the new from the old crater, had disappeared, probably owing to landslides. Fumaroles were found in the crater rim in the gap leading down to the Larikai valley and also one somewhat more to the east above the head of the Rozeau valley.

Professor LACROIX made the ascent along with Madame LACROIX, Ensign DEVILLE, Professor HOVEY, and the Rev. T. HUCKERBY of Chateau Belair, on March 3, 1903, *i.e.*, before the last considerable eruption, and has published his observations in the 'Annales de Géographie.'† The following is an abstract of the parts of his paper which relate to matters that have occurred since the May eruption. He mentions that banks of hot ash and terraces still remain in the Wallibu valley, and that steam explosions still occasionally take place from them.‡ These banks render the river valleys somewhat narrower than before. He saw from his boat, when off the mouth of the Richmond River, an explosion of hot mud take place from the crater of the Soufrière, and he observed the sudden descent of a torrent of mud in the high Rozeau valley, probably caused by a shower. At a height of about 600 metres the ground was covered by large lapilli, the product of the eruption of September, and ejected blocks and bombs were common. They were often partly buried in the lapilli into which they had fallen. He mentions the gap at the head of the Larikai ravine, and was informed by Mr. HUCKERBY that it had been enlarged by the eruption of October, 1902. Avalanches were falling from the walls of the crater, and there was a talus at their base. Large ejected blocks of old rock were more common at the rim of the crater, particularly at the east, than they were lower down. At first, when M. LACROIX gained the edge of the crater, the water of the lake was tranquil, and had the appearance of yellow steaming mud. The least agitation of any part caused it to assume a more grey colour. Suddenly from the centre of the lake there rose a mass of mud of inky blackness, entangling blocks of rock.

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* These measurements appear to have been carefully made. HOVEY gives 600 metres; most of the other observers also give figures, but as they are merely estimates I have not quoted them.

† "Les Dernières Éruptions de Saint-Vincent," Mars 1903, A. LACROIX, 'Annales de Géographie,' tome xii., 1903, No. 63 du 15 Mai 1903.

‡ They appear to have ceased about this time.

After some seconds it reached to the level of the edge of the crater, and then rose to a height of several hundred metres. M. LACROIX succeeded in taking a photograph* which shows an outline like sheaves of rockets, mixed with puffs of white vapour, which soon gained predominance and hid the rest from view. The mass of mud, which rose noisily, fell heavily back again with a deafening roar. Then a new column of vapour, larger than the former, rose from the bottom of the crater and filled it.† The party received a heavy shower of mud. Several other explosions of different degrees occurred while the members were on the summit. The explosion was seen from Castries in St. Lucia, and was sufficiently conspicuous to cause inquiries as to its nature to be made by telegraph.

Professor HOVEY was one of the same party who visited the crater on March 3, 1903, and he crossed the mountain to the windward side a few days later. He remarks‡:—"Considerable alterations have taken place since my former visit 8 months previously. The eruptions of May had left the leeward side coated with a deposit of very fine-grained material, which formed a cement-like mud under the influence of the rain; but the deposit on the windward side was of a coarser nature. Now, the surface to leeward is covered with gravel which has more or less completely hardened into a compact surface. This gravel is composed not only of small fragments from a quarter to half an inch in diameter, but also of numberless bombs. These bombs vary in size from that of a pea upwards, the largest observed were between 2 and 3 feet across. On the windward side the gravelly deposit had not been compacted, but is soft to walk upon. Within the district from Richmond to Windsor Forest on the leeward, no vegetation is to be seen except such as has sprung up along the sides of the gullies which cut through the new deposit into the old soil. On the windward side the slopes of the mountain have been much more generally freed from ash than on the leeward, and considerable vegetation is to be seen on the slopes of the ravines and gorges. The crests of the ridges and the lower slopes, however, are still covered with a coating of bare ash." He mentions the rapidity with which erosion has taken place since the eruption, and estimates the amount that has been carried out to sea from the valley of the Wallibu alone at 25,000,000 tons, without counting that from the surrounding slopes.

Eruption, March 21 *to* 30, 1903.—The Rev. T. HUCKERBY writes as follows§:—"From the 15th to the 18th of March the heat was intense. At 5 o'clock of the morning of the 18th three lunar halos were visible. On the morning of the same day a halo circled the sun. At about 9 o'clock the same night we were disturbed by

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* LACROIX, 'Montagne Pelée,' pp. 53–54 and 176–7, Plates 21, 22.

† LACROIX, 'Montagne Pelée,' Plate 22.

‡ 'Sentry,' St. Vincent, March 1903. 'American Museum Journal,' July 1903. 'Comptes Rendus,' ix., Congrès Géol. Internat. de Vienne, 1903, "The 1902–3 Eruptions of Mont Pelée, Martinique, and the Soufrière, St. Vincent," by EDMUND OTIS HOVEY.

§ Letter to Dr. ANDERSON.

very loud detonations, the earth trembled severely. I immediately went outside, to see if the Soufrière were showing any signs of an eruption. Everything seemed calm and quiet on the northern end of the island, but looking in the direction of the harbour (Chateau Belair), I noticed three horizontal rings of vapour, one within the other.* "On the 21st large volumes of steam were emitted from the crater, and early the following morning detonations and rumblings were heard. At 7.25 a.m. the explosive period of the eruption commenced, the usual black cloud, cauliflower in shape and fringed with various colours, rose to a tremendous height and then passed away in all directions. The regular detonations and explosions ceased about 10 o'clock. Occasionally, during the day, noises proceeded from the crater, as if some great monster were in distress. There were three earthquakes between 7 and 8 in the morning, and one at 9 o'clock. After the detonations and explosions had ceased, the crater continued to send forth dust-laden vapour, without cessation, right on to the 30th of March. On the last-named date I visited the coast as far as the Larikai valley. Very little ejecta had fallen at Wallibu. At Morne Ronde there was a depth of 4 inches of new grey dust. At the opening of the Larikai valley there was a fall of 6¾ inches. Further along the coast, at the bottom of the Larikai ravine, there was a depth of 20 feet of new ejecta, indicating that there must have been a considerable flow from the western lip of the crater. A bomb, found in a heated condition on the top of a deep layer of ash, proved to be 75 lbs. in weight. Between 8 and 9 o'clock on the night of the same day the whole of the crater seemed as if it was lighted up by electricity. I concluded that the bottom of the crater was in a luminous condition and reflected its glow on everything around and on the cloud above. The light lasted for a few minutes and was followed by the ordinary emissions of dense clouds of steam.

"On the 31st I started on a trip round the island. I found that the material distributed on the windward side of the island was very different from that which had fallen on the leeward side. The deposit on the leeward side, except in the Larikai ravine, was consistently grey dust, while on the windward side, ash, pumice, and large pieces of dull chocolate-coloured material preponderated. The pumice, which I had picked up at Owia, has the appearance of a pink sponge.

"At the beginning of April I again visited the Soufrière. The inside of the crater presented an entirely different appearance, the bottom was filled up to about the old water level, with chocolate-coloured ash. In the centre of this new deposit was a comparatively narrow hole, which I concluded was the mouth of the funnel. The southern lip had been raised by the outflowing dust. A large portion of the north-eastern wall had been blown out and a fair number of fissures, which had formed in the new deposit of the crater, were throwing up a large amount of steam.

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* Two such concentric rings were also seen at Chateau Belair on August 30, 1902, before the eruption of September 3.—(Mr. CHASTENET, quoted by Mr. MACDONALD in a letter to Dr. ANDERSON.) See also the eruption of October 13, 14, *supra*.

"I have made many visits to the Soufrière since the occasion mentioned above. The hole in the centre of the new deposit has gradually widened, and, I suppose, will ultimately take up the whole width of the bottom of the crater. Conditions are rapidly becoming normal, and in a few years' time the mountain will once again be covered with verdure and beauty."

Mr. POWELL[*] reports, on March 24, that the depth of black dust was about half an inch at Park Hill. At Three Rivers and Mount William it was about three-quarters of an inch deep and coarser in grain. It contained many considerable pieces of an inch and upwards in size. The cocoa trees were here a good deal damaged. At the experiment station, near Georgetown, it was coarser still, more cinder-like, and pieces of 3 inches or more in diameter were common. The sugar-canes and other plants were much injured. At Dickson's Village, which is in an exposed position above Georgetown, the ash was 2 to 3 inches deep and larger cinders more abundant still. From Georgetown northward the country "presented one blackened waste." At Turema, about 5 inches of dust were measured. On the whole, there appears to have been a light fall of dust over all the island south of Georgetown and Chateau Belair, a moderate fall on the leeward coast north of this, except in the Larikai ravine, where there was a deposit, in places, 20 feet thick; and a fairly uniform layer of a few inches thick over the Carib country, north of Georgetown. The heat-absorbing properties of the last fall were considered to render it more detrimental than the deposits of the former eruptions.

The dust was carried by the wind to Barbados. On Sunday, the morning was clear till about nine, when a dense black cloud came rolling up from the west, the surface wind being easterly at the time. Dust began to fall about 11.15 and it continued to do so more or less heavily up to about 1 o'clock, after which it slackened and ceased altogether at 5 o'clock. When the gloom was deepest, the day was darker than on either of the previous occasions of a fall, viz., the 7th of May and the 16th of October, 1902. During the midday service lamps were lighted in the various places of worship. The dust appears to have taken about two hours in traversing the distance of 111 miles. The amount as estimated by Mr. LEWTON BRAIN and Mr. R. D. ANSTEAD, of the Imperial Department of Agriculture, from observations made at Bay Mansion, was 2½ tons to the acre. It will be remembered that the total fall on May the 7th was 17·58 tons per acre, and that on October 16 about 3·92 tons per acre. The cloud appeared to be denser towards the north, and at Codrington House, two miles to the north of Bridgetown, the fall was 6·52 tons per acre.[†] Since this eruption the crater has been practically quiescent.

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[*] Curator to the Commissioner of Agriculture.

[†] 'Agricultural News,' March 28, 1903, No. 25.

Montagne Pelée in Martinique.

When we visited Martinique in 1902, it was "our intention to make merely such reconnaissances as would enable us in a general way to ascertain the points of difference and of similarity between the outburst of Mont Pelée and that of the Soufrière, and to see what light the phenomena in Martinique threw on the events which had happened in St. Vincent,"* and this being understood, we had the advantage of a friendly conference with Professor Lacroix, the Chief of the French Commission, who most courteously discussed his observations and conclusions with us. These he has since embodied in a monumental volume published by the Academy of Sciences,† and we have already indicated the chief points of difference and similarity between the two volcanoes, both in the preliminary and full report, so that it now only remains to compare the history of the two volcanoes since the great eruption, and to note the changes which, during a visit in March, 1907, I observed to have recently taken place in the crater and the slopes of the mountain, especially the region of the Rivière Blanche, and, since Professor Lacroix's great work is not very accessible to English readers, to draw attention to one or two of the most remarkable phenomena described in it.

The Crater and the Spine.—The great spine which has formed so peculiar and novel a feature in the eruption of Montagne Pelée had no counterpart in the Soufrière of St. Vincent, and this constitutes the most important difference between the outbreaks of the two volcanoes, which in other respects were so remarkably similar. When we visited Martinique in 1902, there was in the upper part of the mountain, at the head of the valley of the Rivière Blanche, a great "triangular fissure,"‡ or **V**-shaped gap, out of which, on July 9, we saw the descent of an incandescent avalanche, which was the counterpart of that which destroyed St. Pierre. Through that gap, as the trade-wind clouds momentarily dispersed, we caught occasional glimpses of a bank of large loose angular blocks of stone at a high temperature, which rolled down at intervals, accompanied by the discharges of volumes of dust-laden steam. We also saw several times for a few moments a large pointed rock, reaching to a height of perhaps 100 feet, or more, above the top of the dome of stones, but as we were ignorant of the exact topography of the locality, which was not accurately marked on the official maps, we could not ascertain for certain that it was more than an unusually large crag on the further lip of the crater, and accordingly did not particularise it in the report. This uncertainty as to the topography has now been cleared up. The map in Professor Lacroix's book (p. 120) correctly represents the

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* Preliminary Report. 'Roy. Soc. Proc.,' vol. LXX., 1902, p. 439; and Part I., p. 478.

† 'La Montagne Pelée et ses Éruptions,' par A. Lacroix, Paris. Masson et Cie., 1904.

‡ Part I., p. 491, called "cleft" in the Preliminary Report, pp. 440, 441, and "Echancreur en V" by Lacroix.

topography as I observed it in March, 1907, and it is now certain that the bank of stones was the surface of a new cone, or dome, which was in process of being built up in the Étang Sec, which, in this eruption at any rate, was the working crater of the volcano.* The dome has never shown any crater of explosion on its summit and appears to be comparable, for instance, to such masses as the Domite Cones of the Auvergne. The pointed rock rose from its summit. It now appears that this rock had been independently seen three days previously, viz., on July 6, by a French party under Professor LACROIX, and by an American party under Professor JAGGAR, and that photographs had been obtained by both, which, though very indistinct, enabled useful diagrams to be drawn.† It is certain that this rock occupied much the same position on the summit of the dome as the spine did later, and one of its surfaces showed "long striated smooth slopes" like the later spine. It does not appear, however, to have been the identical spine, for its smooth surface faced westward instead of eastward, as did the corresponding surface of the latter. JAGGAR thinks it was an early stage of the same phenomenon; LACROIX thinks, on the contrary, that it was part of a "bourgeonnement" (budding) of lava (LACROIX, p. 41) and that its shape was due to the splitting off and falling away of the surrounding portions, and this view is supported by the craggy condition of the summit of the dome shown in photographs taken in October before the upraising of the spine, which commenced in earnest in November.

The French Commission commenced systematic observations from the Morne des Cadets early in October, using first an alidade and then a theodolite, and on November 3 the measured height of the summit was 1343 metres (4406 feet). LACROIX considers that the growth of the spine commenced on the night of the 3rd to 4th November, 1902,‡ and on November 24 it had reached a height of 1575 metres (5167 feet) above sea-level, or a growth of 230 metres in 20 days, *i.e.*, at the average rate of over 10 metres a day. This was the first maximum height; from that time a series of falls gradually reduced the total height till February 6, 1903, when only 1424 metres (4672 feet) were registered, or a net loss of 151 metres (495 feet), and this in spite of a continued rise of the remainder of the spine. From February 7 a new period of growth commenced, though less rapid than the former; on March 25 the former maximum of 1575 metres was again reached and soon surpassed, and from May 10 to 31 and from June 25 to July 6 the height was continuously above 1600 metres (5249 feet). The absolute maximum reached was 1608 metres (5276 feet) on July 4, 1903, or 257 metres above the former summit of the mountain, and

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* The other small lake on the summit, the Lac des Palmistes, if a crater at all, was not in action in 1902, and its place is now occupied by a plain of *débris* and ejected blocks, including many bread-crust bombs.

† LACROIX, p. 114. JAGGAR, "The Initial Stages of the Spine on Pelée," 'American Journal of Science,' vol. xvii., January, 1904.

‡ LACROIX, *loc. cit.*, p. 121 *et seq.*

about 600 metres (1969 feet) above the former level of the crater lake of the Étang Sec from which it sprung.*

This cone or dome appears to have been formed of viscous lava partially or wholly solidified in places, and this mixture would be in a condition, by the sudden disengagement of the vapour and the shattering of the partially solidified rock, to give rise to, or at any rate take part along with, other discharges from the chimney in the formation of the incandescent avalanches and other forms of "nuées ardentes"† which have been observed. The avalanche seen by us certainly contained a number of large blocks of a brighter red colour and apparently of a higher temperature than the rest of the material in it, and these presumably had come from the dome. LACROIX considers that the "nuées ardentes" observed by him proceeded from the surface of the dome, and especially from a patch on its south-west flank near the base. They did not issue from any well-marked crater on its summit.

The spine itself seems, as we might have expected, to have been formed of very similar material to the dome. LACROIX speaks of a carapace, or shell, on its surface, which often was detached in flakes (fendillement), disclosing an interior at a high temperature which he describes as consisting of porous matter with driblets (bavure) of molten lava exuding from the intervals and cracks. Portions were frequently detached with the emission of "nuées ardentes." There was no great central passage. The surface of the spine was scratched and grooved by friction against the walls of the volcanic chimney out of which it rose. Its shape at first was angular, but it was almost cylindrical in its later stages, probably because the prominences in the chimney were gradually worn off, and its diameter was estimated by LACROIX at 150 metres. He calculates that if the spine had not undergone any crumbling and falling (ecroulement) between November 3, 1902, and July 4, 1903, it would have attained an altitude of at least 2200 metres (7218 feet), and the total height of the column extruded must have been about 850 metres (2789 feet), or, say, 2800 feet.‡ The careful measurements regularly taken showed that it diminished in height solely by flaking and falling, and that at no time did it sink again into the chimney when it had once risen. It appears clear, therefore, that both the dome and the spine were formed by molten matter, with perhaps some inclusions of blocks torn from the walls of the passage, being forced up from below into the volcanic chimney, that this matter was at first sufficiently plastic to spread out and form the dome, and that as cooling gradually took place, parts solidified and broke up into large blocks, from some of which the vapours escaped

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* These estimates depend on earlier measurements, the accuracy of which cannot be depended upon to within a few metres.

† The term "Nuées ardentes," as used by LACROIX, appears to include both the "Incandescent Avalanches" and "Black Clouds" described in Part I. He now prefers the term "Nuée Peléenne" as more general. ('L'Éruption du Vésuve en Avril 1906,' p. 12, par A. LACROIX; 'Revue Générale des Sciences des 30 Octobre et 15 Novembre 1906.') Both Dr. FLETT and I prefer our old terminology as more precise.

‡ LACROIX, 'Montagne Pelée,' p. 132.

quietly, while other parts exploded into minute fragments with sudden escape of vapour and descended the mountain as "nuées ardentes," accompanied often with a mixture of the larger fragments. It is impossible to say exactly the depth to which this breaking up and liberation of the vapours extended. As the whole gradually cooled and became consistent, and as further material was forced up from below, the upper portion no longer spread out into a dome, but was forced up "en masse" as a spine, though it still retained veins of pasty or liquid material spreading through it. This forcing up from below by fluid pressure was clearly the main mechanism of the ascent, but LACROIX thinks that the pressure of the veins of semi-fluid lava might be an accessory cause of the ascent and especially of the lateral swelling and flaking off of the crust. It is impossible to deny the existence of this cause, since it has been postulated that the dome was formed in this way in the early stages of the eruption, but it clearly became much less important later on. Some authors have suggested that the spine was an old plug formed in the chimney, by the materials left there at the close of an earlier eruption. There is no proof whatever of this theory and it does not accord well with the transition from the formation of the dome to that of the spine, nor does it account for the high temperature of the central parts of the spine with its veins of still semi-fluid lava, or for the flaking off of the crust and emission of "nuées ardentes" as the veins of lava came to the surface.

I made two ascents of the mountain in March, 1907, and on the second occasion the cloud lifted for a few moments and enabled me to get a photograph which showed the stump of the spine rising out of a cone of talus surrounding it, and obviously formed of its ruins (Plate 24). At the line of junction of the spine and the talus was a ring of very active fumaroles from which steam and other vapour was escaping with a loud roar, obviously from under considerable pressure. The clouds closed in again before it was possible to complete the examination, but the photograph shows the spine to consist of a sort of volcanic agglomerate of blocks of various sizes, similar to what I imagine the structure of the dome to have been.

The Wall of the Crater.—The talus extended in every direction up to the walls of the crater, and had in a great degree filled it up. On the south-west side was the above-mentioned V-shaped gap where the talus had overtopped the former crater ring and extended down to the valley of Rivière Blanche. On the east and south-east the crater was least filled. Its wall continued uncovered from the side of the gap to beyond the remains of Morne Lacroix, to an average depth of probably above 100 feet. It was almost vertical throughout all this extent. The valley formed between it and the talus appeared to extend, but at a decreasing depth, round the north of the dome.

The resemblances between the valleys of the Wallibu in St. Vincent and the Rivière Blanche in Martinique, and the phenomena observed in those valleys respectively, are summed up in Part I., p. 489, and the changes which have since occurred serve chiefly to increase the resemblances and minimise the differences. Thus in March, 1902, there was in the latter valley a number of fumaroles, some of which were active enough to have led to the supposition of their being parasitic craters. Further examination has satisfied Professor LACROIX of their superficial nature, *i.e.*, their origin in the deposits of hot ash, and their consequent similarity to those in the Wallibu.* They are all now cool and extinct except one group, which I had the pleasure of visiting in company with M. GUINOISEAU, Adjutant in charge of the Observatory of Morne des Cadets. They are situated at a height of about 1350 feet above the sea, on the low ridge between the Rivières Blanche and Claire, which here flow down one broad valley apparently much in the same way as two rivers often occupy each one side of a big old valley in St. Vincent. The ridge itself is perhaps 50 feet higher than the valley on each side, and broad in proportion. It consists of fragmentary ejecta of the 1902 eruption, including a good many large blocks. The temperature of the fumaroles had been as high as 300° C. last year, but was gradually decreasing. M. GUINOISEAU found it to be about 230° C. at the time of our visit. This group is the only one about the nature of which any doubt now exists, but it appears most probable that its origin, like that of the others, is superficial.

The differences between the two valleys are not by any means so great as the resemblances, and they appear to be all traceable to two causes, viz., the repeated, or rather, the at one time almost constant, passage of the incandescent avalanches, and the fact that owing to the configuration of the crater these all descend through the V-shaped gap right down the valley on which they spend their whole force. Thus the denudation of the deposits is in a somewhat less advanced stage than in the Wallibu, and the bedding somewhat more complicated owing to an alternation of water-sorted beds with those of fresh ash. Moreover, apparently owing to the very direct course of the valley from the V gap to the sea, and its steep inclination, the number of large ejected blocks even in the lower part of the valley is much greater than in the corresponding part of the Wallibu. This is only what might have been expected when I recall the stones which we saw descending by leaps and bounds in the incandescent avalanche of July, 1902. They were large enough to be visible at a distance of several miles and distinctly a brighter red than the rest of the avalanche material.

In this connection also ought to be mentioned another phenomenon, which though not altogether absent in St. Vincent is much more conspicuous in Martinique, viz., a scoring and grooving of the rocks of the sides of the Blanche valley. The part I specially noticed was a cliff nearly 200 feet high in the ridge between the Blanche and Sèche Rivers and perhaps half a mile nearer the sea than the active fumaroles above mentioned. The valley here is somewhat narrower than higher up, and much narrower than lower down, and it is just the part where the avalanches might be

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* LACROIX, p. 400.

expected to attain their greatest speed. The whole rock is scored and grooved in a way recalling glacial scratches, but I have scarcely ever seen any due to that cause so well marked. These scratches, I since find, have been noticed by LACROIX and HOVEY in other parts of the valley.* The rock is a tuff containing many blocks of very hard andesite, so many that it might almost be called an agglomerate. The body of the tuff itself, on the contrary, in which the blocks are embedded though tenacious is soft enough to be cut with a knife, yet the hard stones have been planed off level with the rest of the mass. Nothing could show more vividly the amount of force applied, and the suddenness of its application.

Owing to the cause previously mentioned very few of the upper valleys received any hot ash, but any which did so present a most striking similarity to those in St. Vincent. Thus a photograph of the upper Rozeau valley in St. Vincent is practically indistinguishable from one of the upper Falaise in Martinique. Both were deeply filled with hot ash in the early stages of the eruption, in which explosions were seen to take place that were supposed to proceed from parasitic craters. In both cases what we see are not really true craters, but merely examples of places where secondary steam explosions took place in the hot ash as previously so often mentioned in the Wallibu district. In Martinique the rains, associated with the eruption, swept down such quantities of coarse débris as to form a delta in a few hours (Plate 25, fig. 4).

The Return of Vegetation.—Vegetation has returned in a manner and to an extent strikingly similar to what has taken place in St. Vincent. Thus, at a height of 1500 feet, on the east side of the mountain, where the ascent is usually made from Vivé, practically all the trees are killed and their trunks remain as bare stumps, while a luxuriant vegetation is growing up chiefly from the old roots (Plate 24). Large sheets of ferns are particularly noticeable. The ferns extend considerably higher, viz., to about 2000 feet, where they give way to grasses, while towards the summit only a few mosses and lichens are found. The slopes above Morne Rouge, as far as could be observed from the road, were in a similar condition. At Morne Rouge village the deserted gardens are full of luxuriant tropical growth, so full that most of the gates cannot be opened; partly no doubt in consequence of being embedded in ash, but principally owing to the new plants, which have grown up since the place has been left to run wild.

At St. Pierre the principal street, along which is one of the chief roads in this part of the island, has been cleared of ash and débris. The ruins of the houses on each side are still embedded in ash and covered by a dense jungle of tropical vegetation.

The valley of the Rivière Blanche and the district between it and St. Pierre is the only part which is still bare of vegetation, and this is no doubt due to the passage down it of the repeated "nuées ardentes."

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* LACROIX, p. 217; HOVEY, 'Preliminary Report,' p. 363.

The General Sequence of Volcanic Phenomena, etc.[*]

In addition to the volcanic and seismic occurrences noticed under this heading, mention ought to be made of the great eruption of the volcano of Santa Maria in Guatemala, on October 24, 25, 26, 1902, news of which had scarcely arrived in Europe at the time when Part I. went to press. Owing to the extremely remote and inaccessible position of the volcano the eruption did not attract the notice it deserved, it was not examined at the time by any English or American man of science, although Professor Karl Sapper, of Tübingen, has published an account.[†]

This eruption was of the same explosive type as those of St. Vincent and Martinique, but much more violent. An entirely new crater about three-quarters of a mile in its longer diameter was formed, and the south side of the volcano (which was supposed to have been extinct) was blown away.

I venture in conclusion to submit the following speculation as to the depth of the volcanic foci beneath St. Vincent and Martinique. The chimneys of the two volcanoes appear to have some connection underground as may be inferred from the following considerations. The eruptions have been repeatedly either simultaneous or so nearly so that the difference in time might be accounted for by the magma being delayed in travelling through a devious and perhaps branching passage or system of passages, blocked in different degrees by various obstructions. The eruptions have been of the same type, viz., explosive without the effusion of lava, and of a rather special variety of that type, the Pelean.[‡] The chemical composition of the ejecta is not more different than could be explained by the interaction between the magma at a high temperature and the walls of the passages, supposing them to intersect various strata. It seems, therefore, natural to conclude that the two volcanoes are at the ends of two branches of one common passage, and it is not unreasonable to suppose that these branches divide at an angle not very obtuse and consequently at a great depth. If the two volcanoes were supplied from a comparatively superficial laccolite or intrusive sheet of molten matter extending widely under the whole district at no very great distance below, why did not an eruption also take place in the Island of St. Lucia, which is in a direct line between the two volcanoes and in which there is an active Soufrière, or through the sea bottom, which attains a depth of 10,000 feet both on the Atlantic and Caribbean side of the chain of islands?

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[*] Part I., p. 532.

[†] Dr. Karl Sapper, 'In den Vulcangebieten Mittelamerikas und Westindiens,' Stuttgart, 1905, and several smaller articles.

[†] I visited and examined the volcano in January, 1907, and have published an account of this visit in the 'Geographical Journal,' April, 1908.

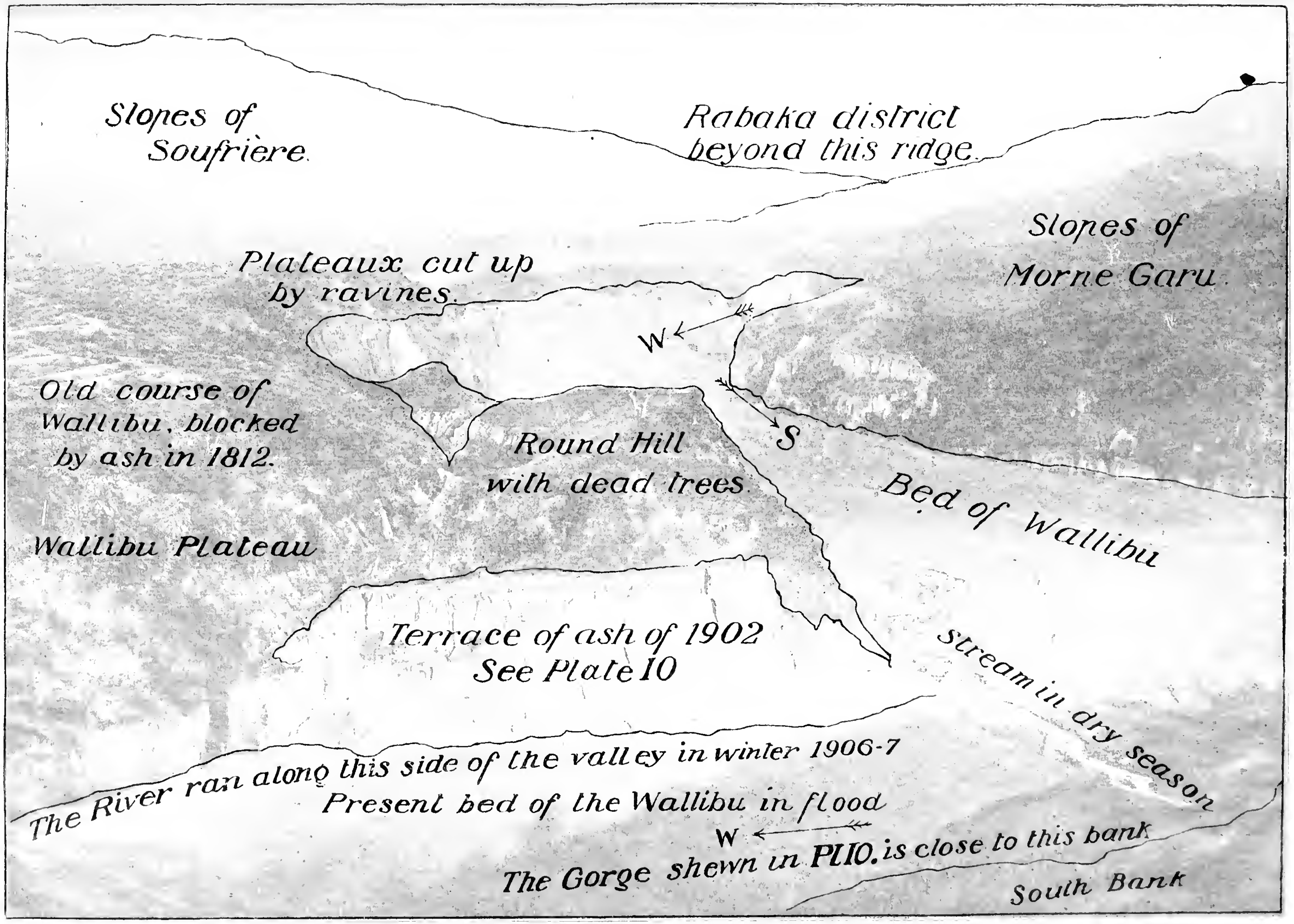
[‡] For a discussion of this see Part I., p. 499, and for the details of the coincidence of these eruptions see p. 532.

LIST OF ERRATA

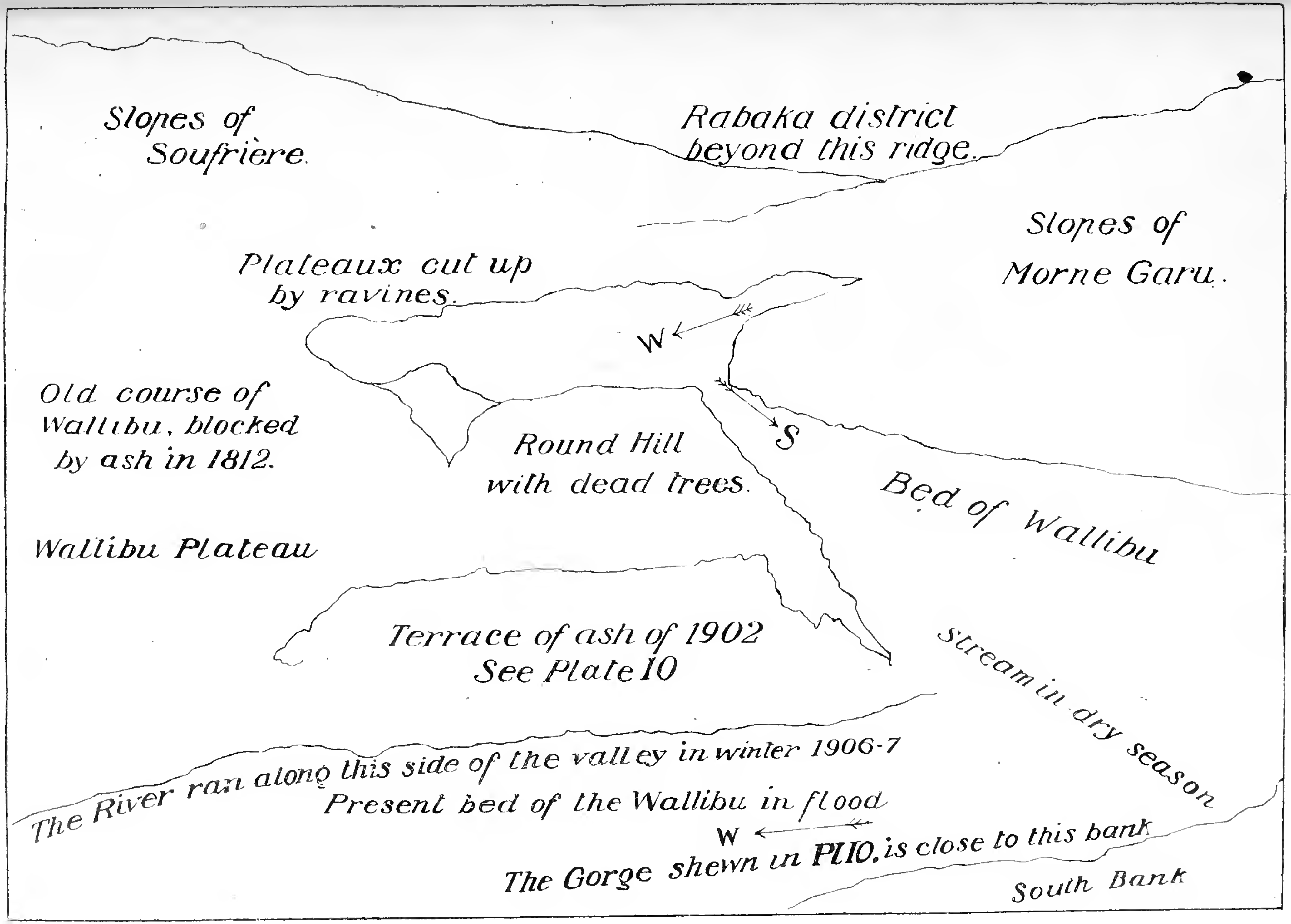
In Part I. ('Phil. Trans.,' A, Vol. 200, p. 353).

Page 361, line 31, *for* "north" *read* "south"
,, 362, ,, 12, ,, "indicates" *read* "indicate"
,, 378, ,, 26, delete brackets ( )
,, 392, ,, 18, *for* "ontburst" *read* "outburst"
,, 393, ,, 28, ,, "sand," *read* "sand"
,, 400, ,, 11, ,, "builing" *read* "building"
,, 404, ,, 30, ,, "Wallibu" *read* "Wallilabu"
,, 406, ,, 5, ,, "Wallibu," ,, "Wallilabu"
,, 407, ,, 26, ,, "where;" *read* "where"
,, 412, ,, 11, delete $\delta\gamma$—
,, 414, ,, 26, *for* "Wallibu," *read* "Wallilabu"
,, 435, ,, 10, ,, "Plate 21," *read* "Plate 31"
,, 452, ,, 12, ,, "pointin goutward" *read* "pointing outward
,, 471, ,, 5, ,, "has" *read* "had
,, 480, ,, 4 from bottom, *for* "p. 11" *read* "Plate II"
,, 497, ,, 5 ,, ,, ,, "on" *read* "in"
,, 509, ,, 6 ,, ,, ,, "The" *read* "the"
,, 532, ,, 9 ,, ,, ,, "Ruez-Altenango" *read* "Quezaltenango"
,, 535, ,, 25, *for* "1776" *read* "1766"
,, 543, ,, 4 from bottom, *for* "Sowtray" *read* "Sowray"

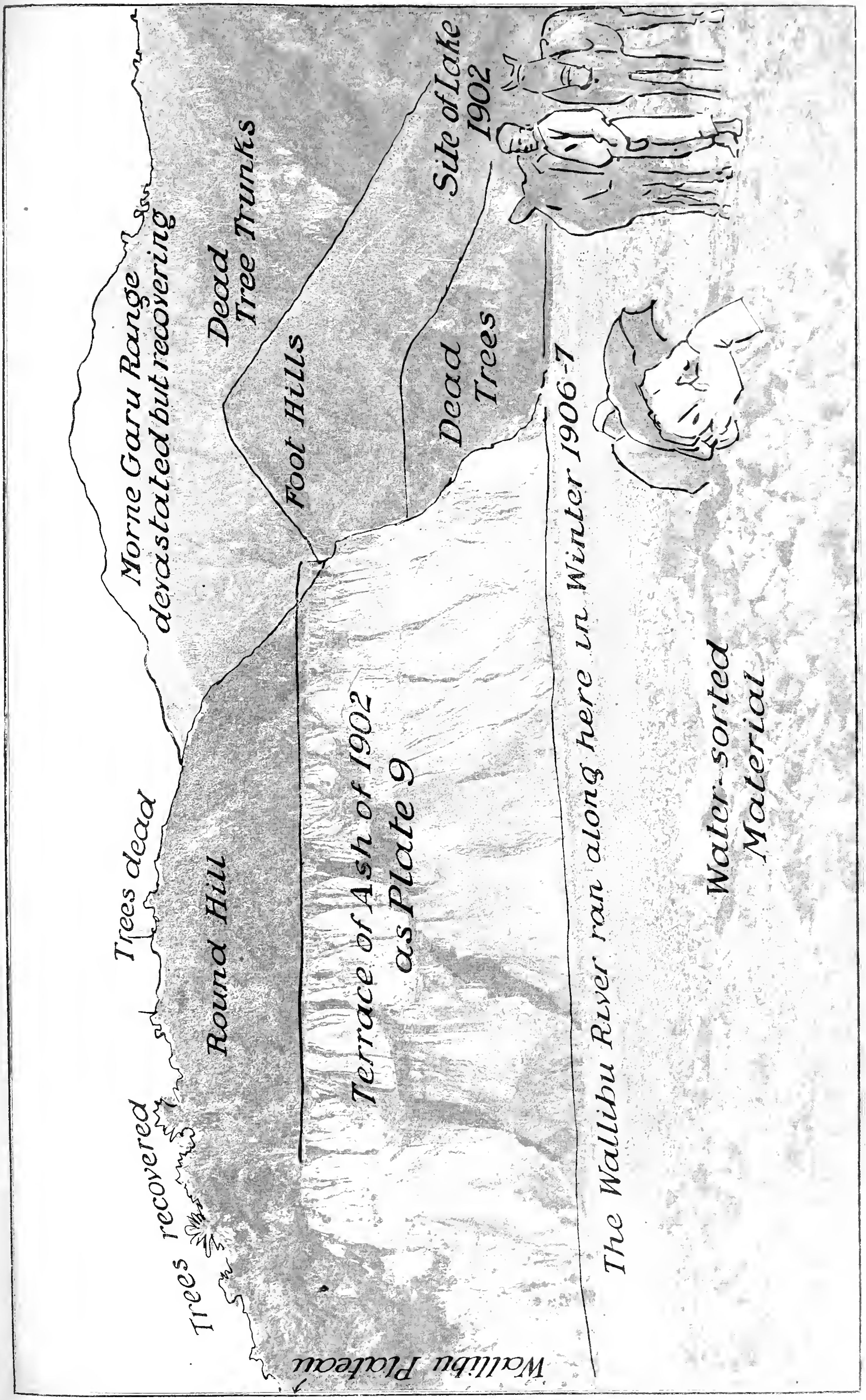
,, 413 is incorrectly numbered 418



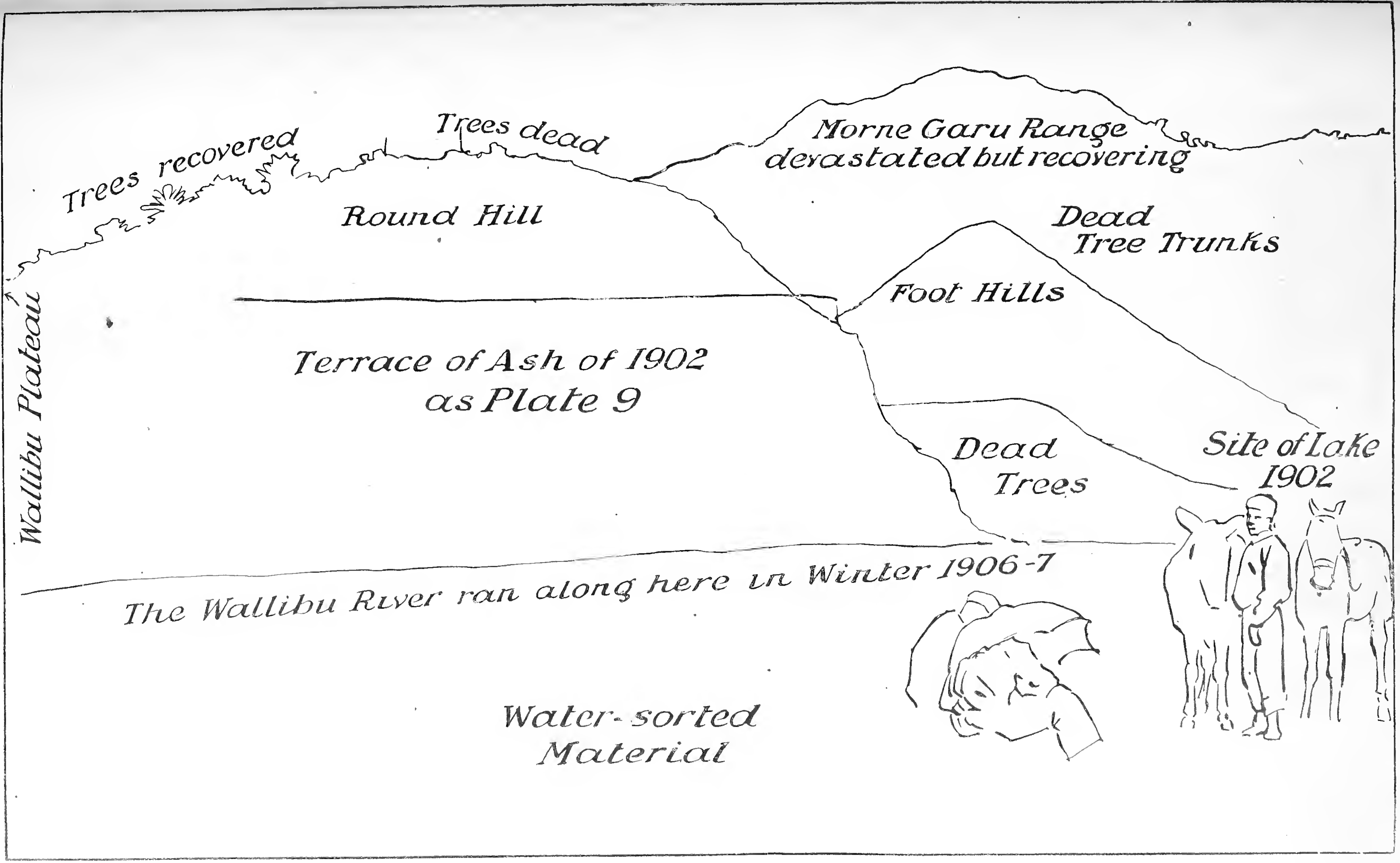
[illegible] Wallibu district, from Richmond Ridge, near [illegible] Hill

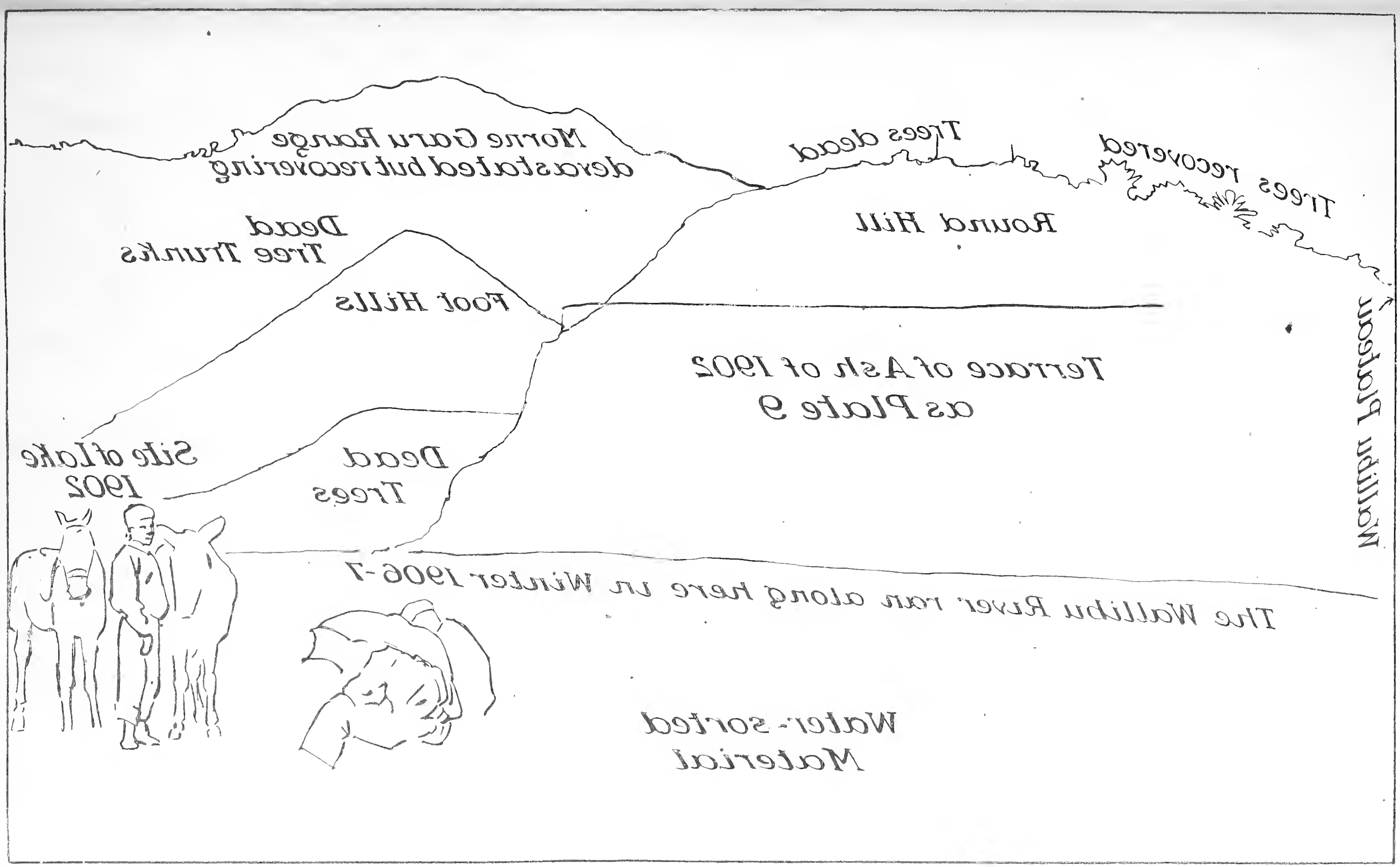

Slopes of Soufrière.
Rabaka district beyond this ridge.
Slopes of Morne Garu.
Plateaux cut up by ravines.
W
S
Old course of Wallibu, blocked by ash in 1812.
Round Hill with dead trees.
Bed of Wallibu
Wallibu Plateau
Terrace of ash of 1902 See Plate 10
Stream in dry season
The River ran along this side of the valley in winter 1906-7
Present bed of the Wallibu in flood
W
The Gorge shewn in Pl.10. is close to this bank
South Bank

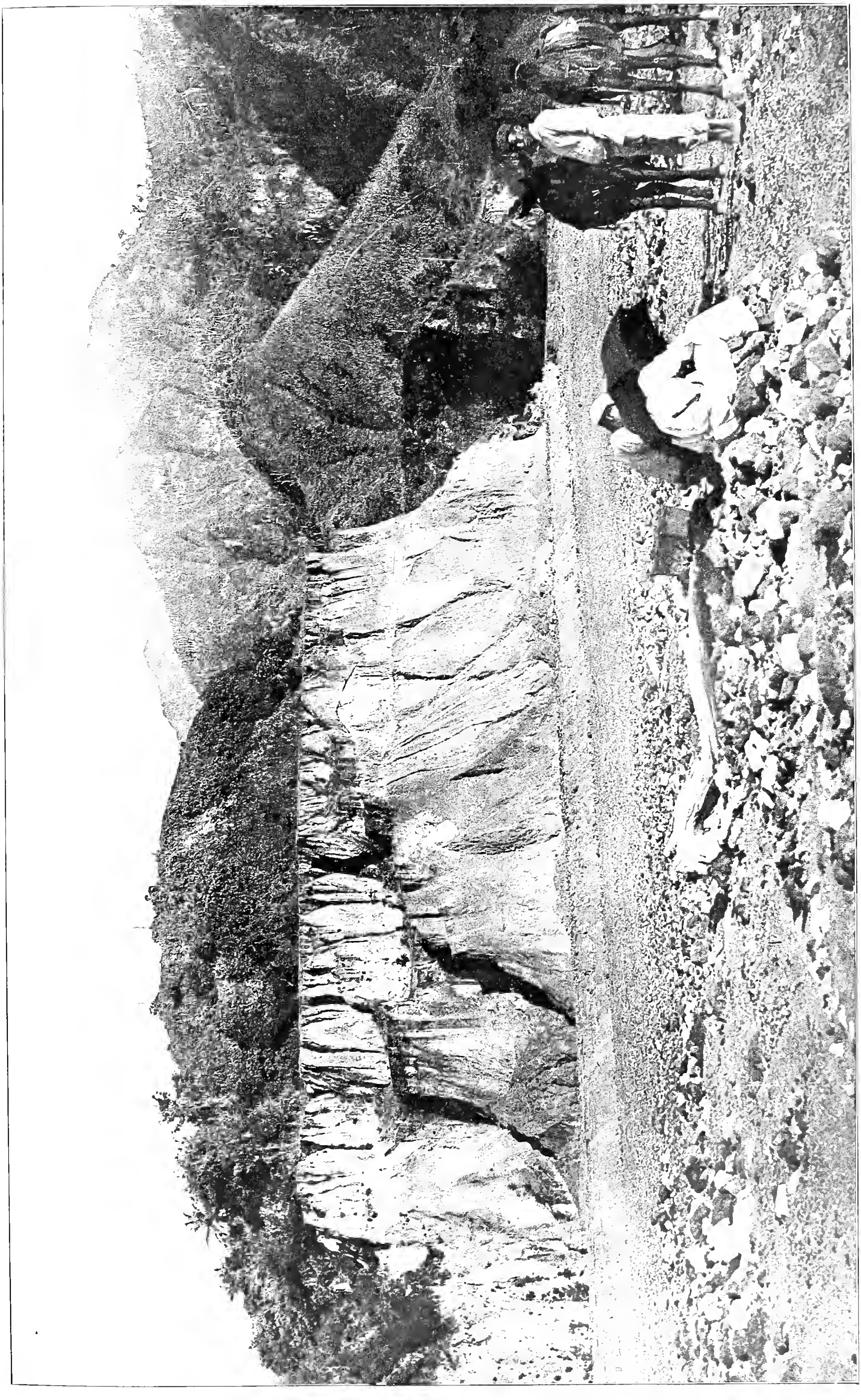
Lower Wallibu district, from Richmond Ridge, near Bunker's Hill.



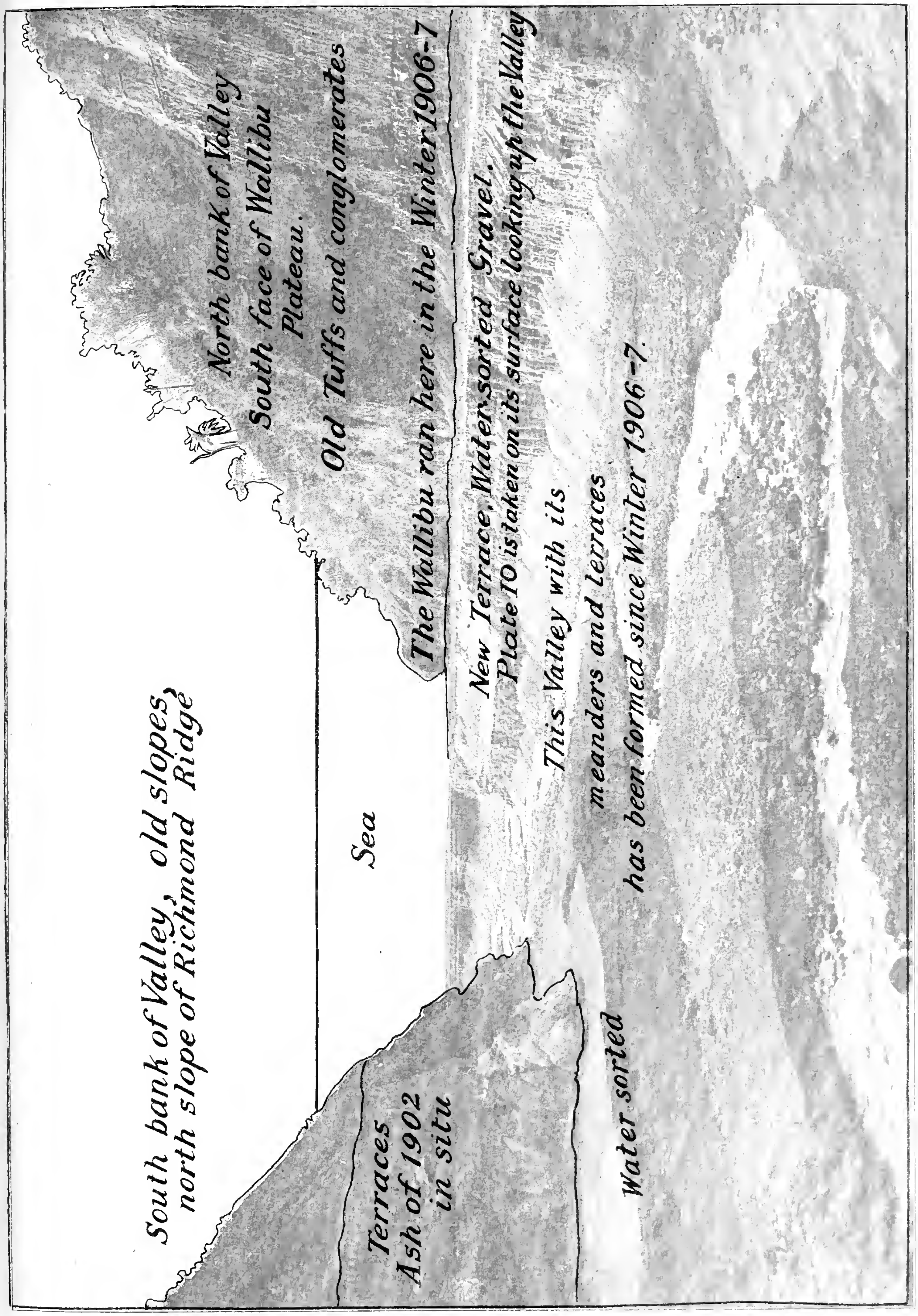
Terrace of new ash, North bank, lower Wallibu Valley.


Trees recovered
Trees dead
Morne Garu Range devastated but recovering
Round Hill
Dead Tree Trunks
Foot Hills
Wallibu Plateau
Terrace of Ash of 1902 as Plate 9
Dead Trees
Site of Lake 1902
The Wallibu River ran along here in Winter 1906-7
Water-sorted Material

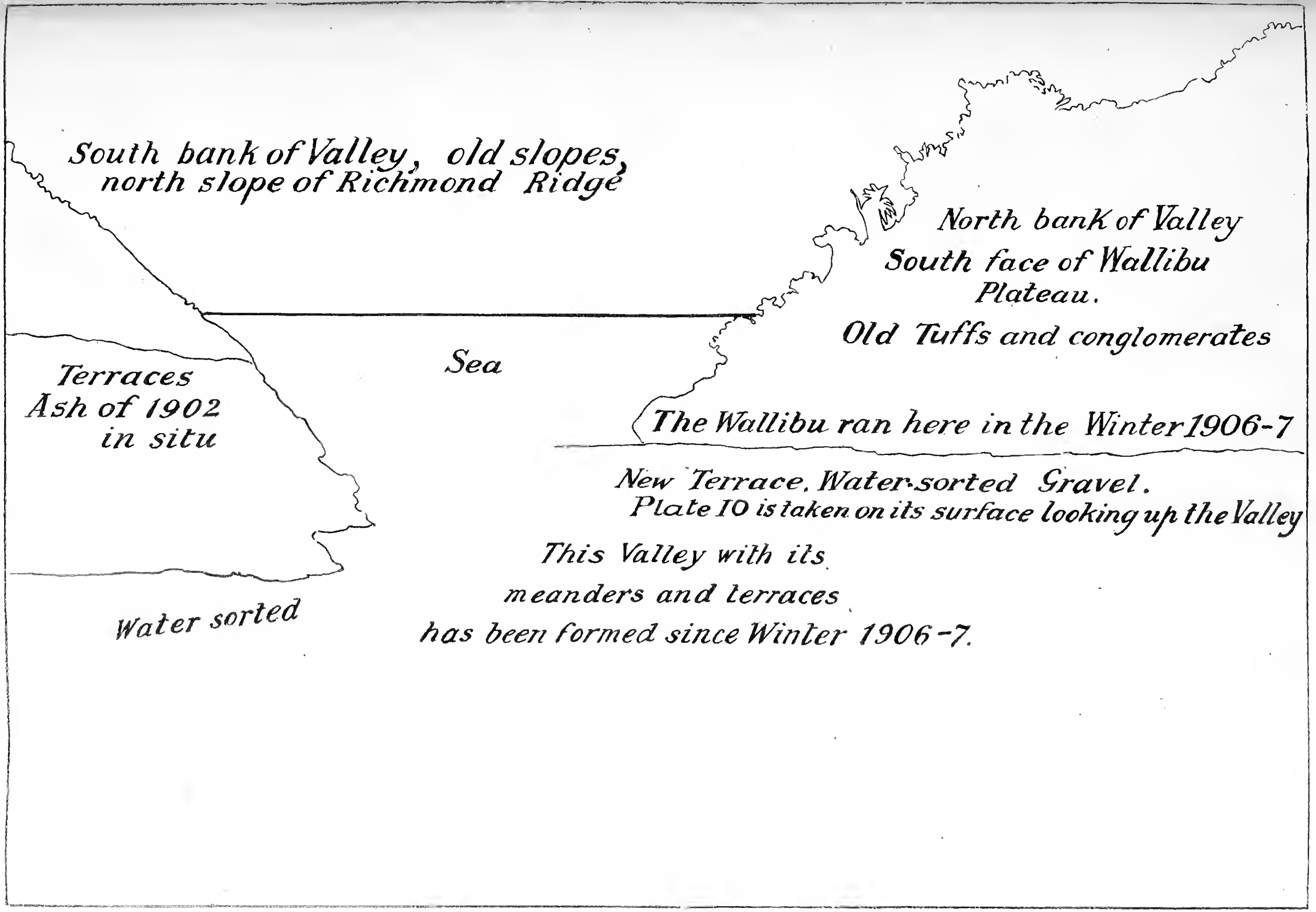

Morne Garu Range
devastated but recovering
Trees dead
Trees recovered
Dead
Tree Trunks
Round Hill
Foot Hills
Wallibu Plateau
Terrace of Ash of 1902
as Plate 9
Site of Lake
1902
Dead
Trees
The Wallibu River ran along here in Winter 1906-7
Water-sorted
Material

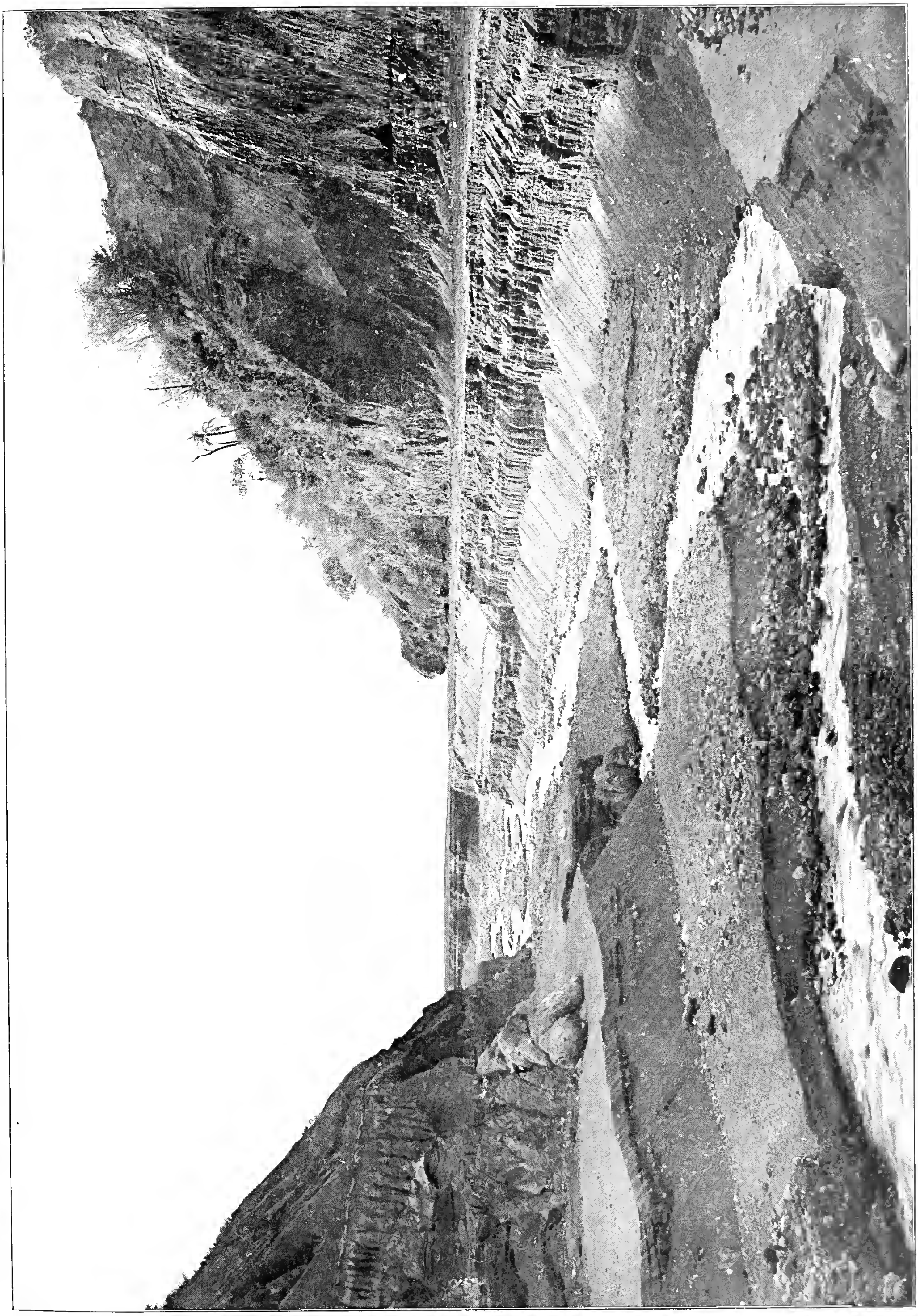


Terrace of new ash, North bank, Lower Wallibu Valley.



Lower Wallibu Valley, looking West, towards the sea.


South bank of Valley, old slopes,
north slope of Richmond Ridge
North bank of Valley
South face of Wallibu
Plateau.
Old Tuffs and conglomerates
Sea
Terraces
Ash of 1902
in situ
The Wallibu ran here in the Winter 1906-7
New Terrace. Water-sorted Gravel.
Plate 10 is taken on its surface looking up the Valley
This Valley with its
meanders and terraces
has been formed since Winter 1906-7.
Water sorted



Lower Wallibu Valley, looking West, towards the sea.

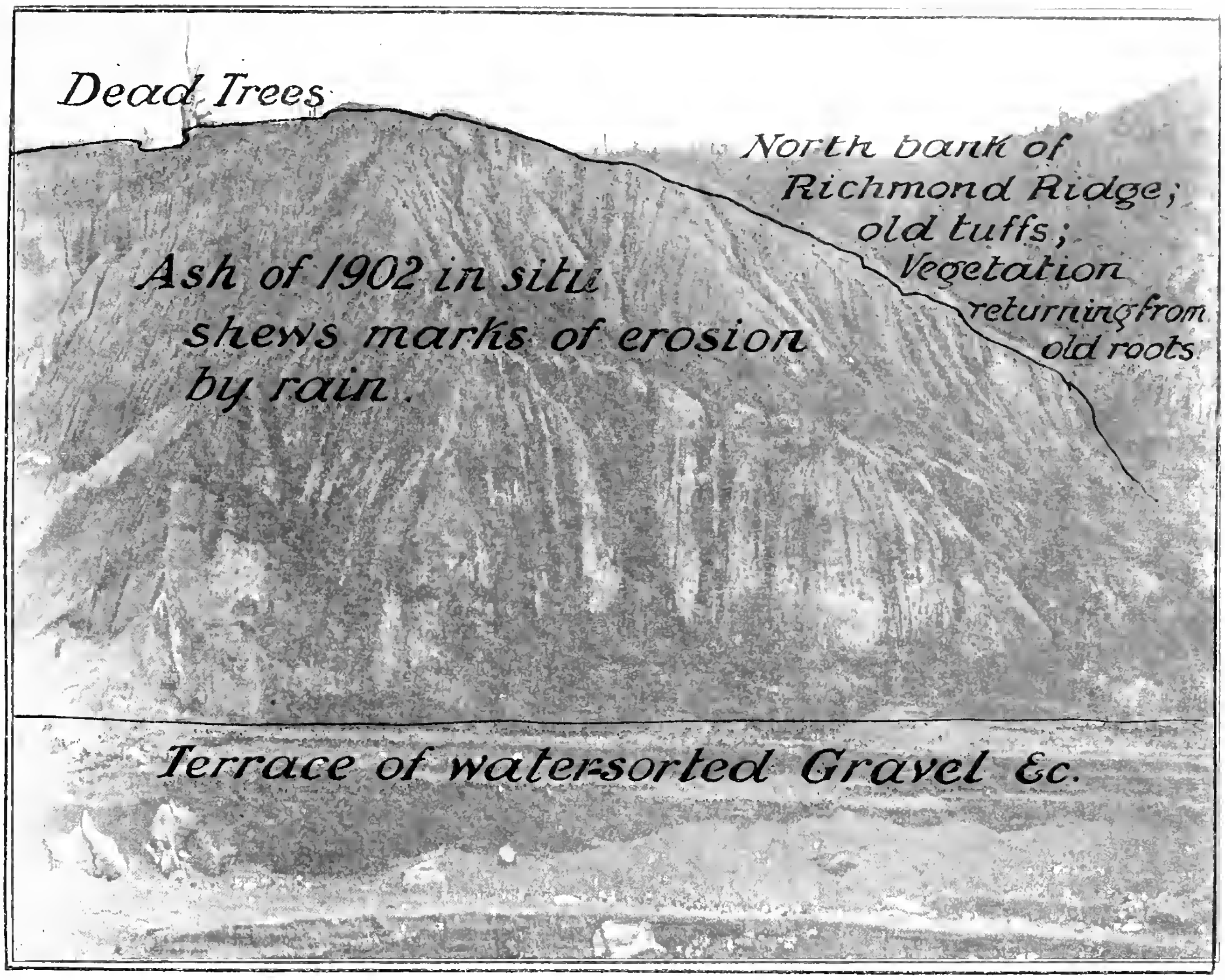


Fig. 1. *Terraces on South bank of Lower Wallibu.*

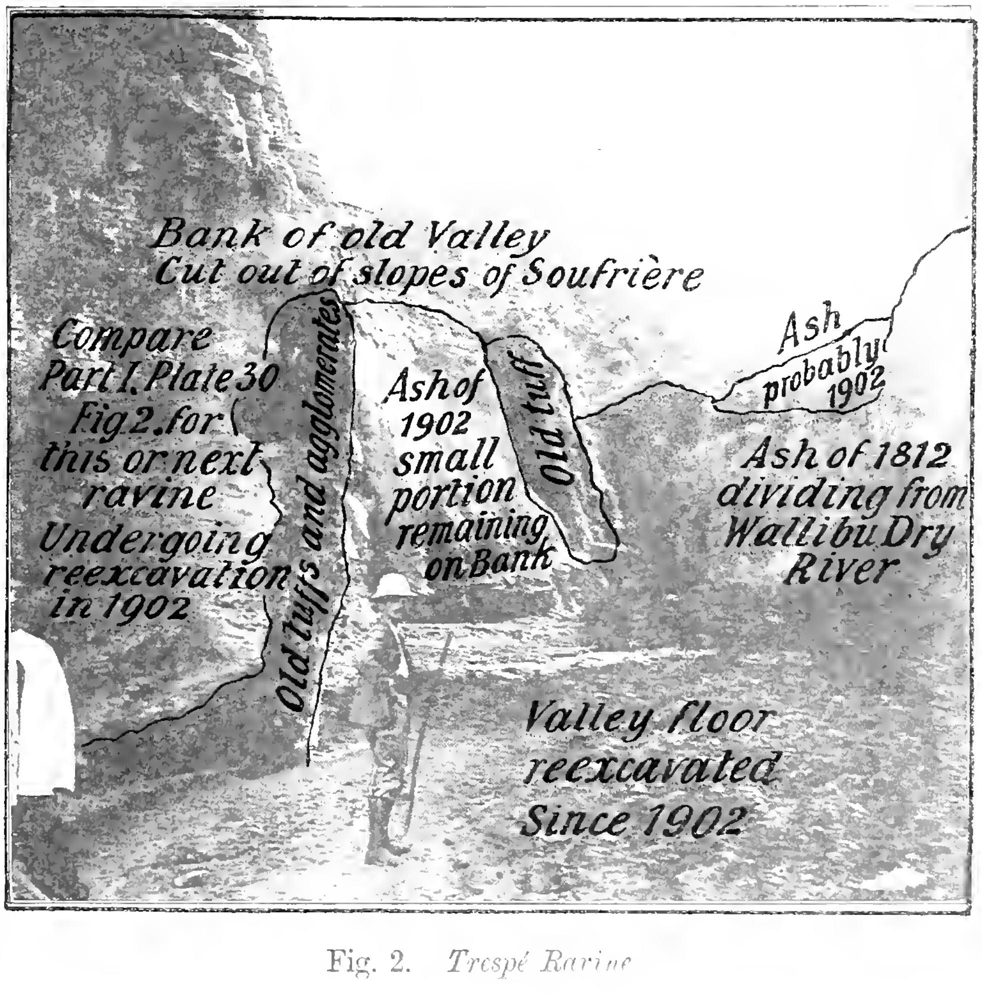
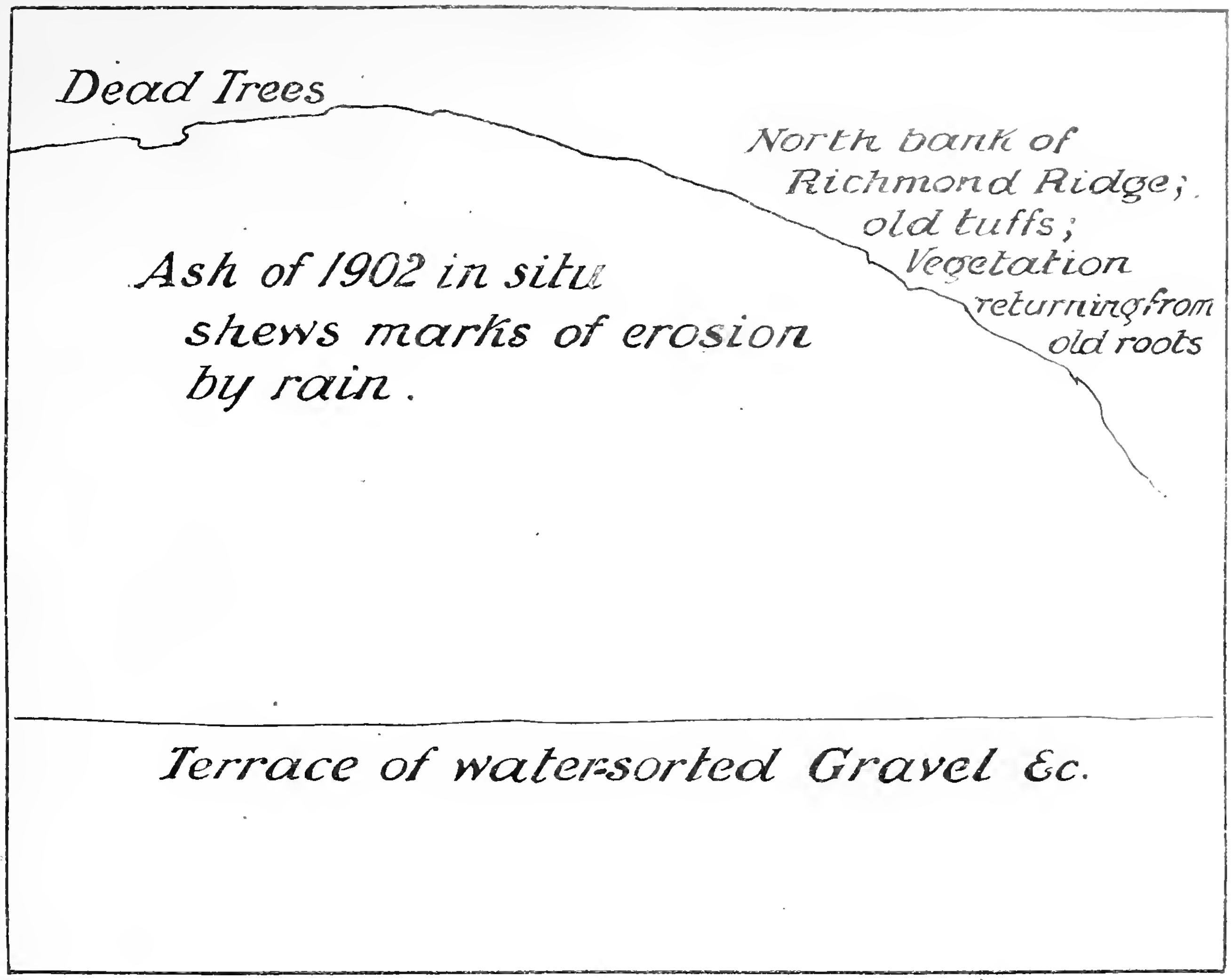
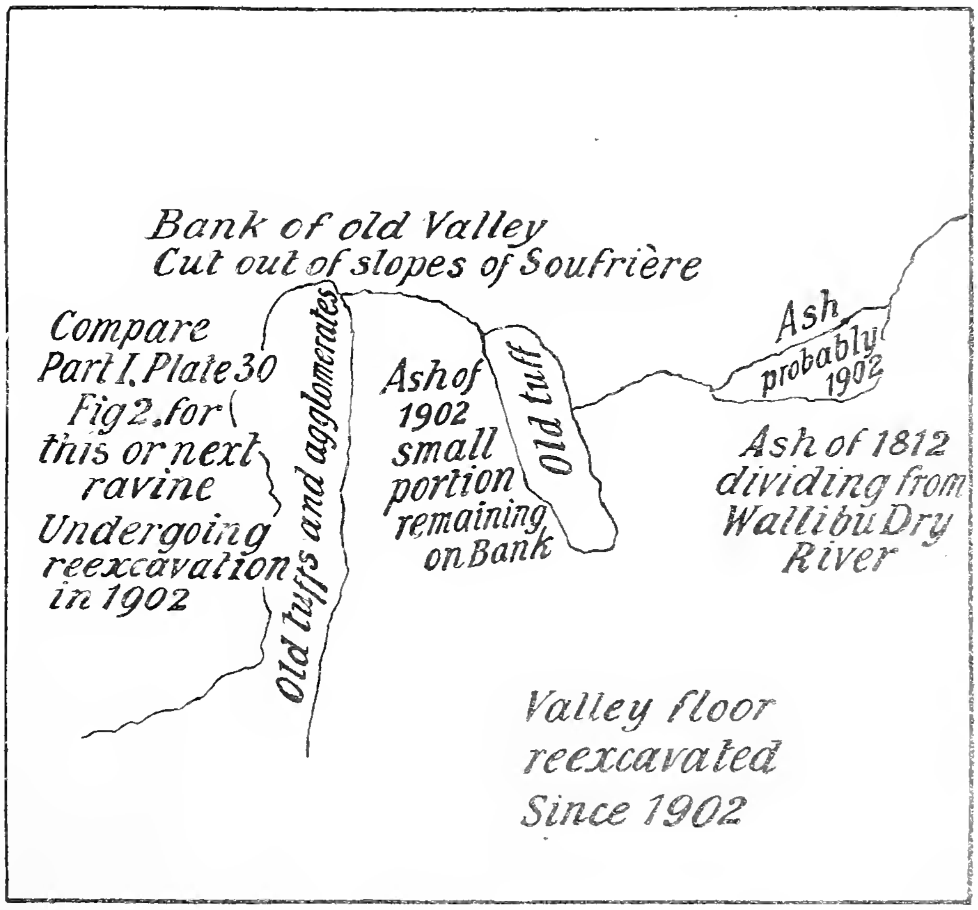
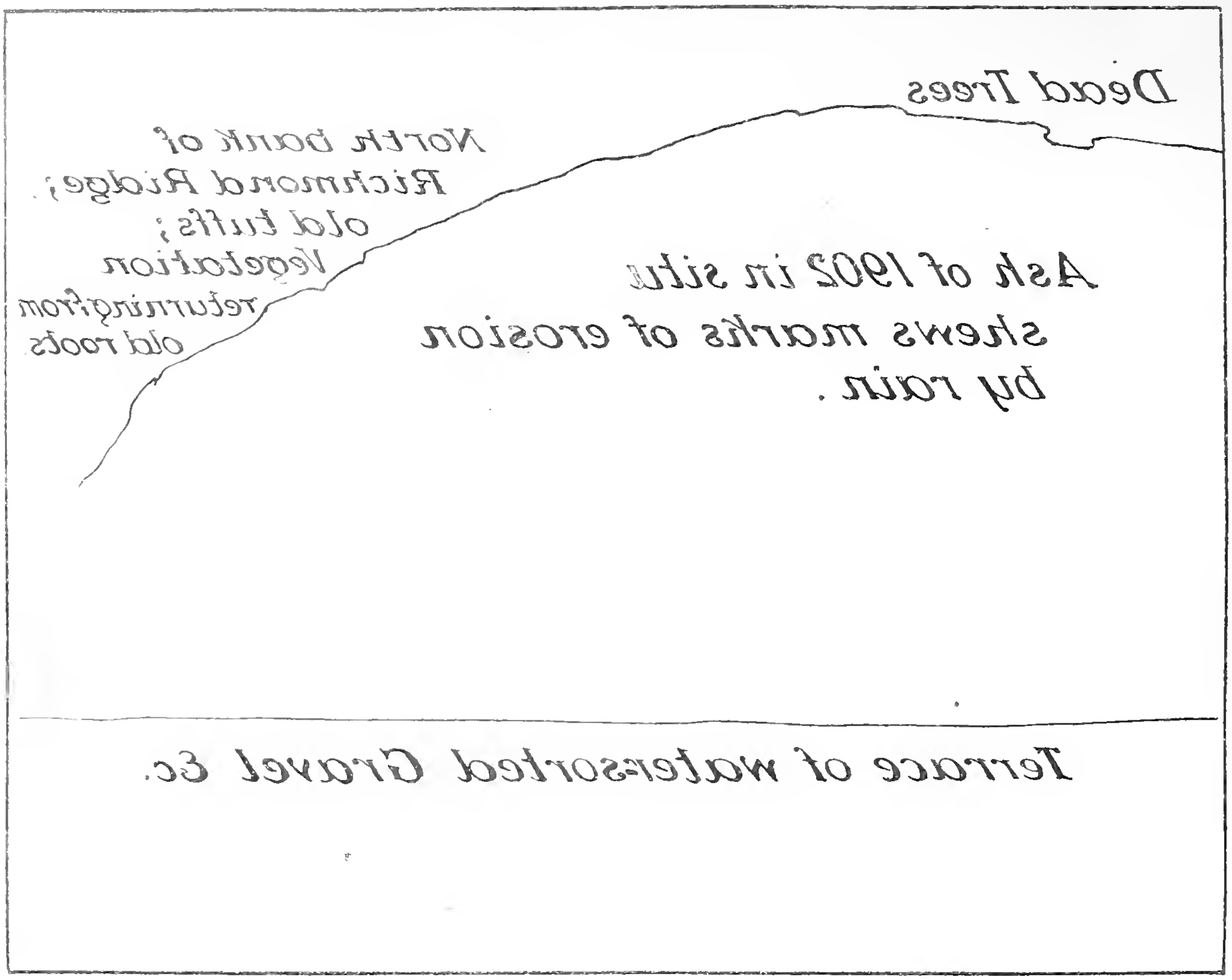


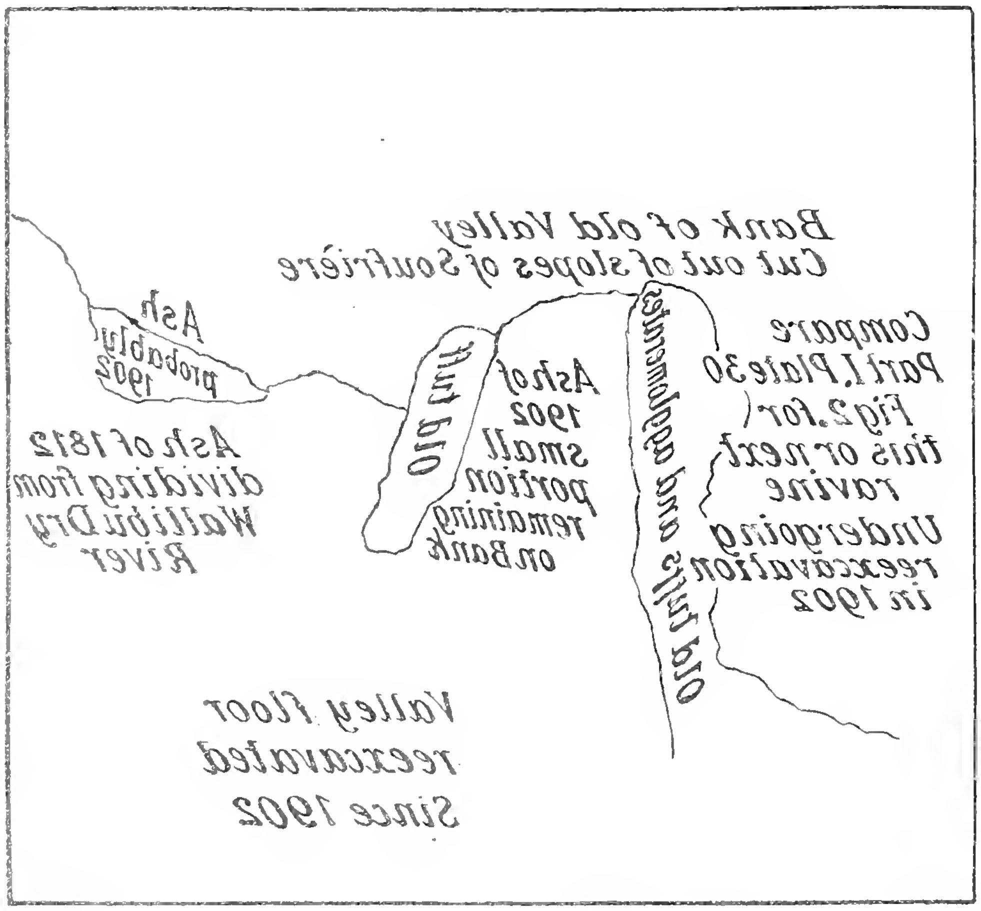
Fig. 2. *Trespé Ravine.*


Dead Trees
North bank of Richmond Ridge; old tuffs; Vegetation returning from old roots
Ash of 1902 in situ shews marks of erosion by rain.
Terrace of water-sorted Gravel &c.


Bank of old Valley Cut out of slopes of Soufrière
Compare Part I. Plate 30 Fig 2. for this or next ravine
Undergoing reexcavation in 1902
Old tuffs and agglomerates
Ash of 1902 small portion remaining on Bank
Old tuff
Ash probably 1902
Ash of 1812 dividing from Wallibu Dry River
Valley floor reexcavated Since 1902



Dead Trees
North bank of Richmond Ridge; old tuffs; Vegetation returning from old roots
Ash of 1902 in situ shews marks of erosion by rain.
Terrace of water-sorted Gravel &c.



Bank of old Valley Cut out of slopes of Soufrière
Ash probably 1902
Ash of 1812 dividing from Wallibu Dry River
Old tuff
Ash of 1902 small portion remaining on Bank
Old tuffs and agglomerates
Compare Part I. Plate 30 Fig 2. for this or next ravine Undergoing reexcavation in 1902
Valley floor reexcavated since 1902

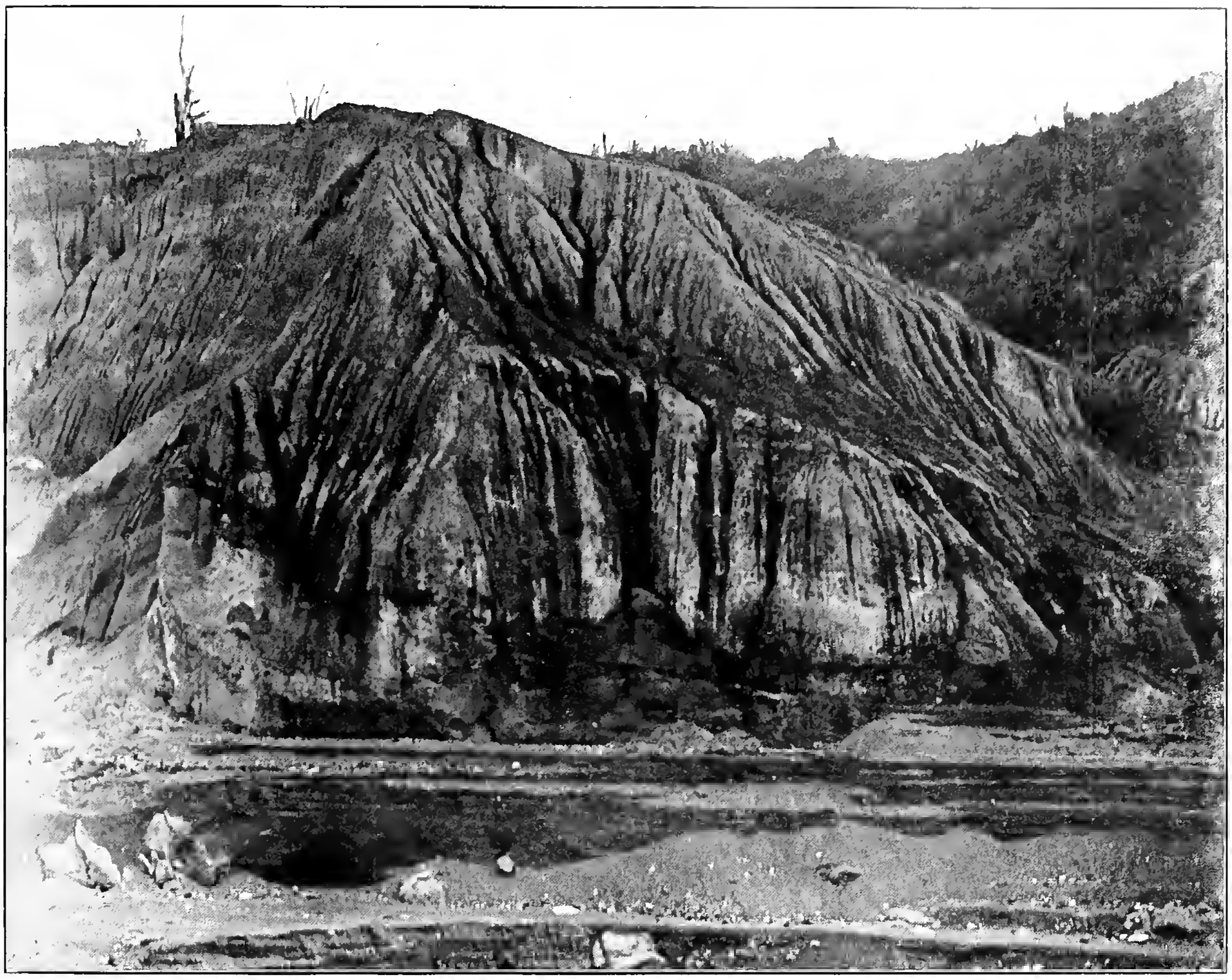


Fig. 1. *Terraces on South bank of Lower Wallibu.*

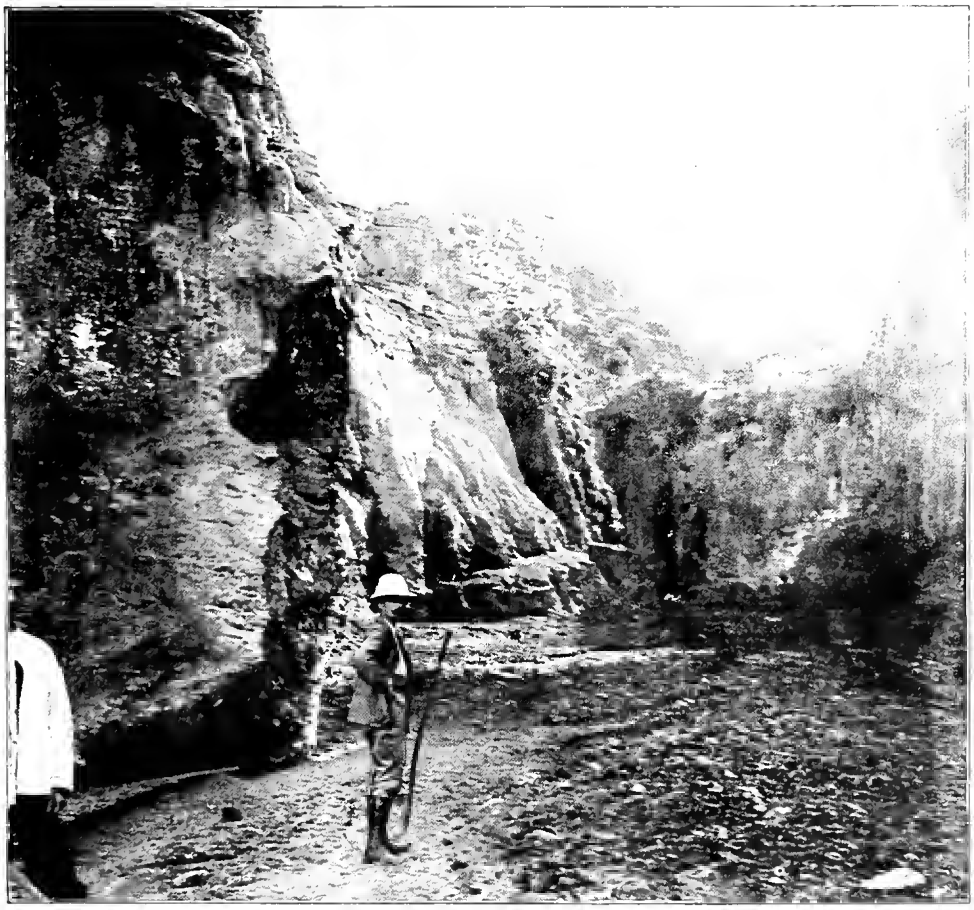
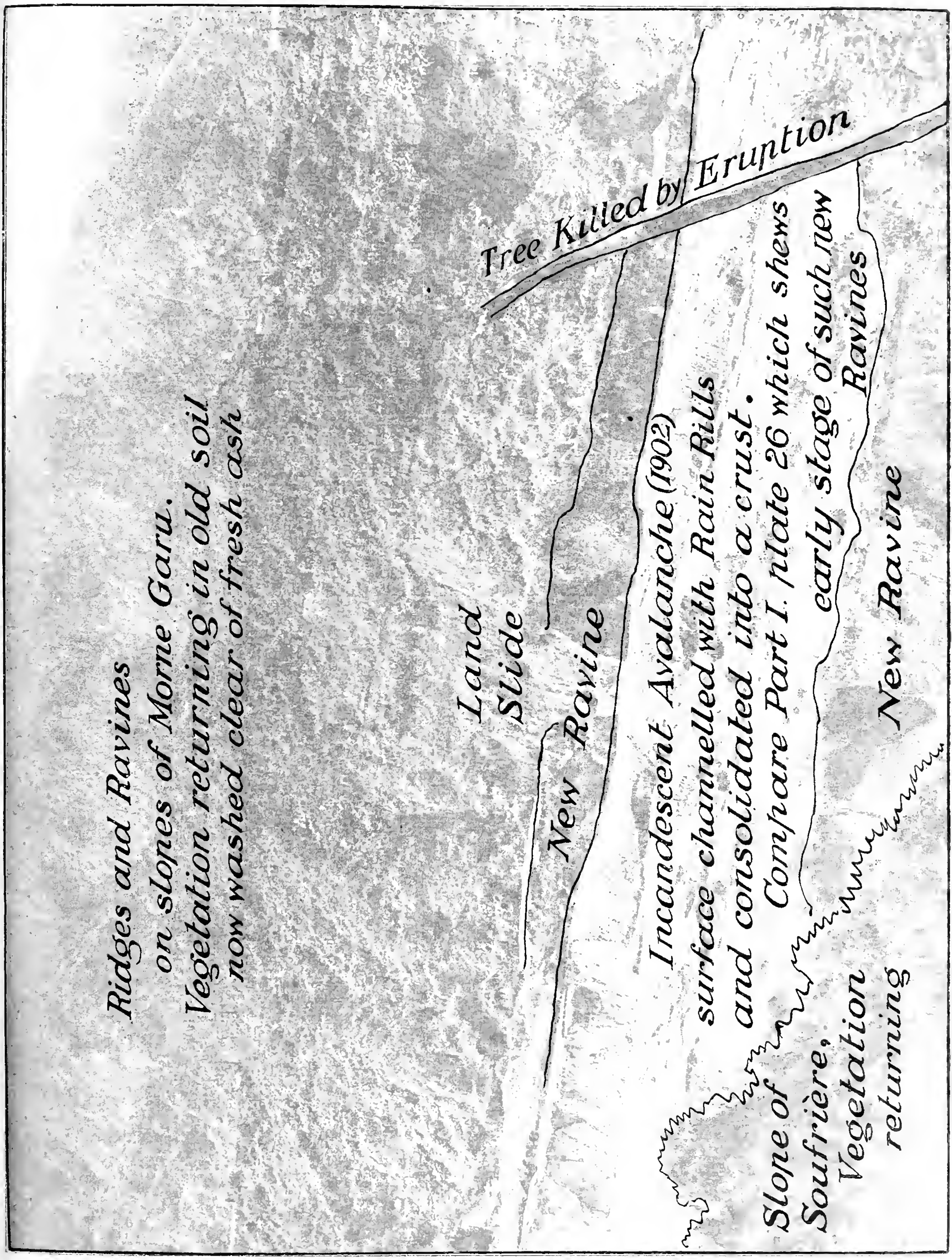
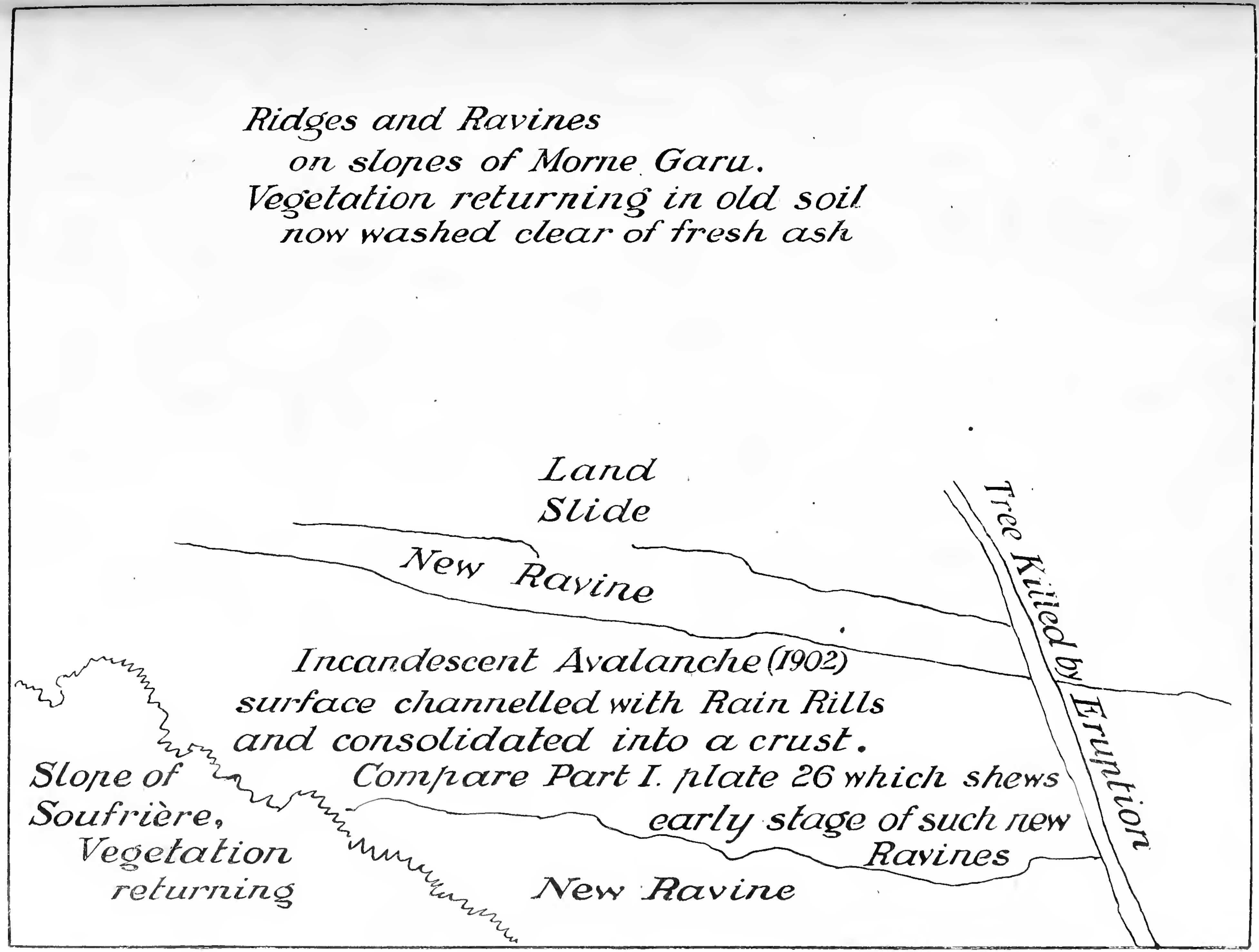
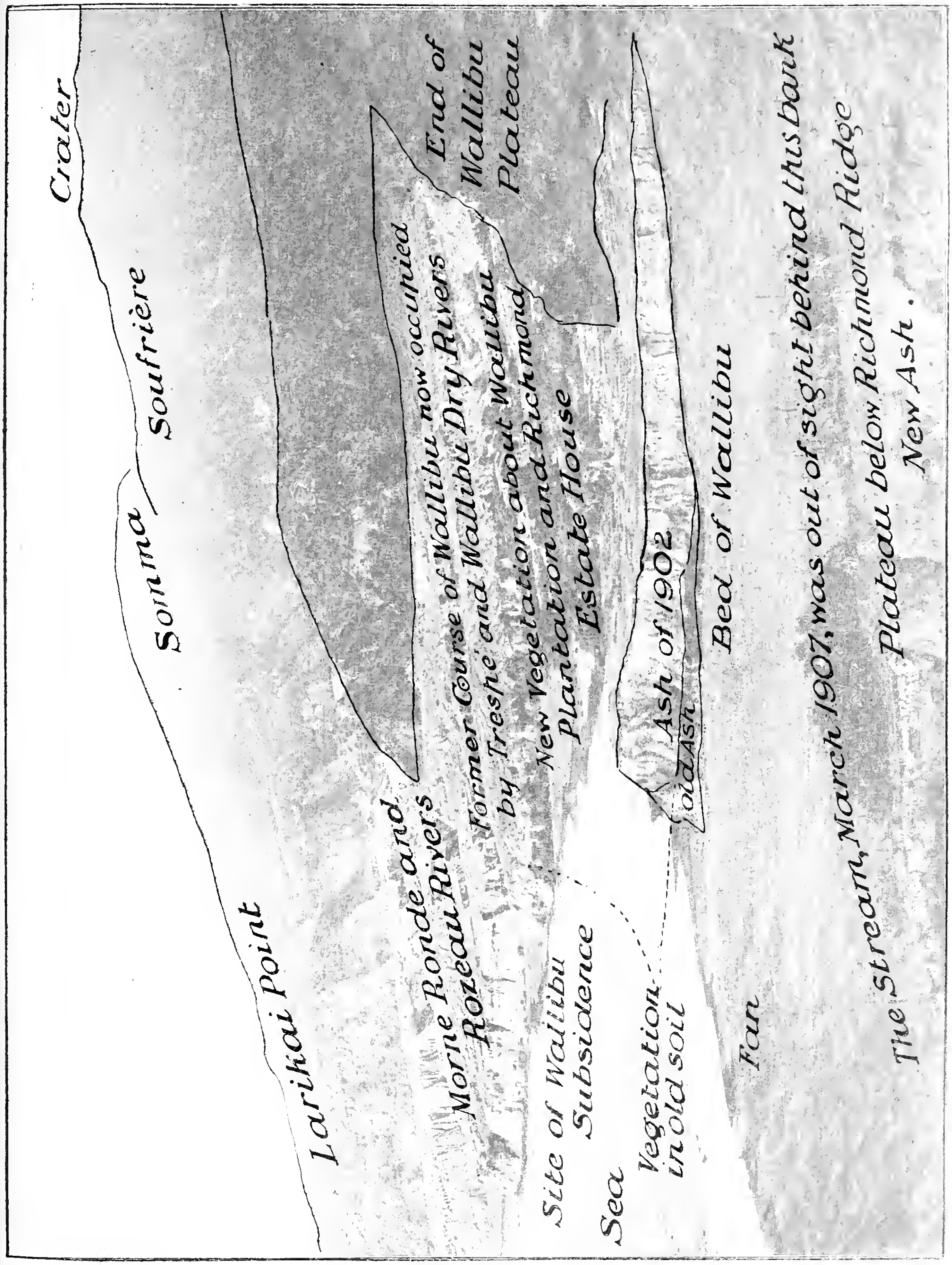


Fig. 2. *Trespé Ravine.*

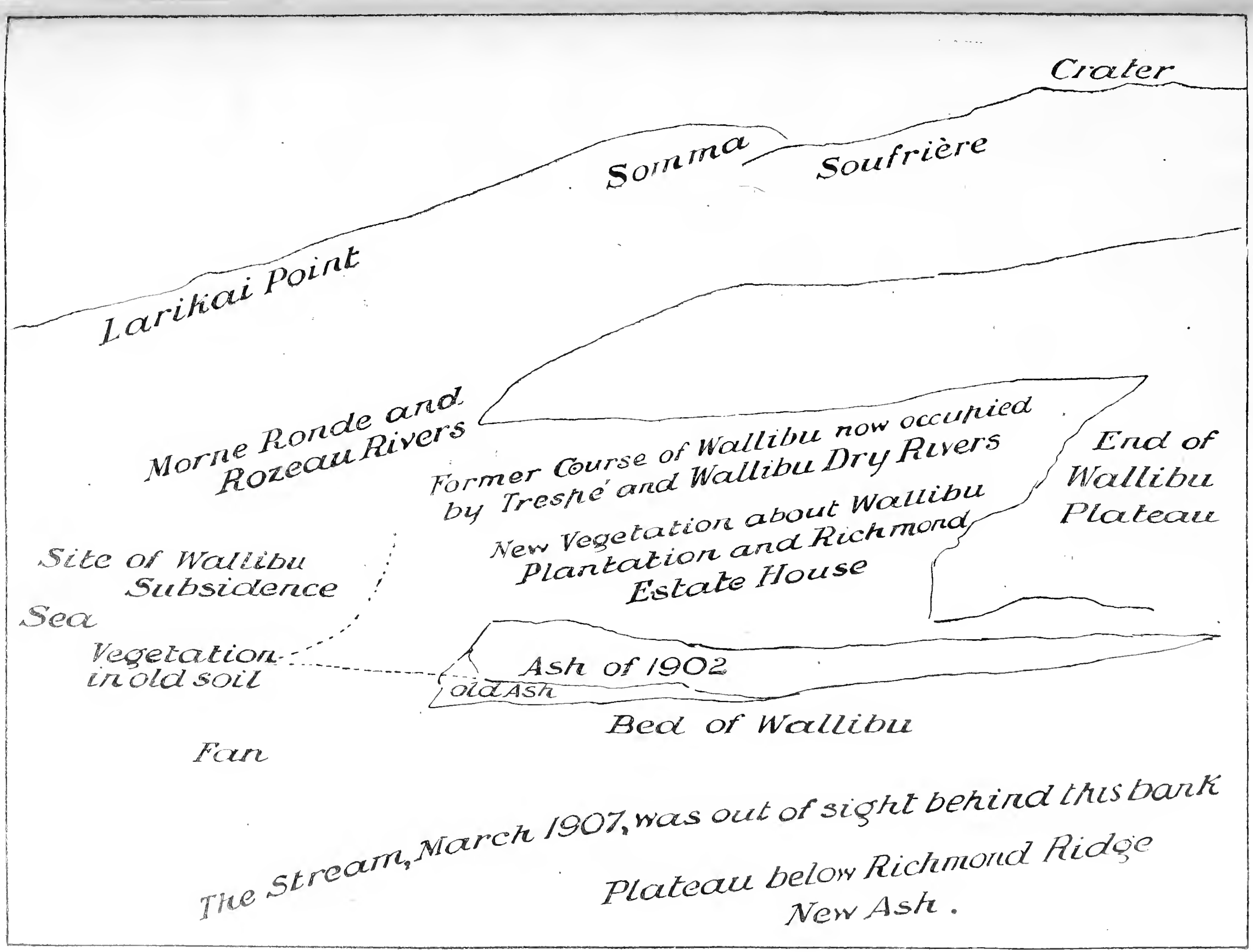

Ridges and Ravines
on slopes of Morne Garu.
Vegetation returning in old soil
now washed clear of fresh ash
Tree Killed by Eruption
Land
Slide
New Ravine
Incandescent Avalanche (1902)
surface channelled with Rain Rills
and consolidated into a crust.
Compare Part I. plate 26 which shews
early stage of such new
Ravines
New Ravine
Slope of
Soufrière,
Vegetation
returning

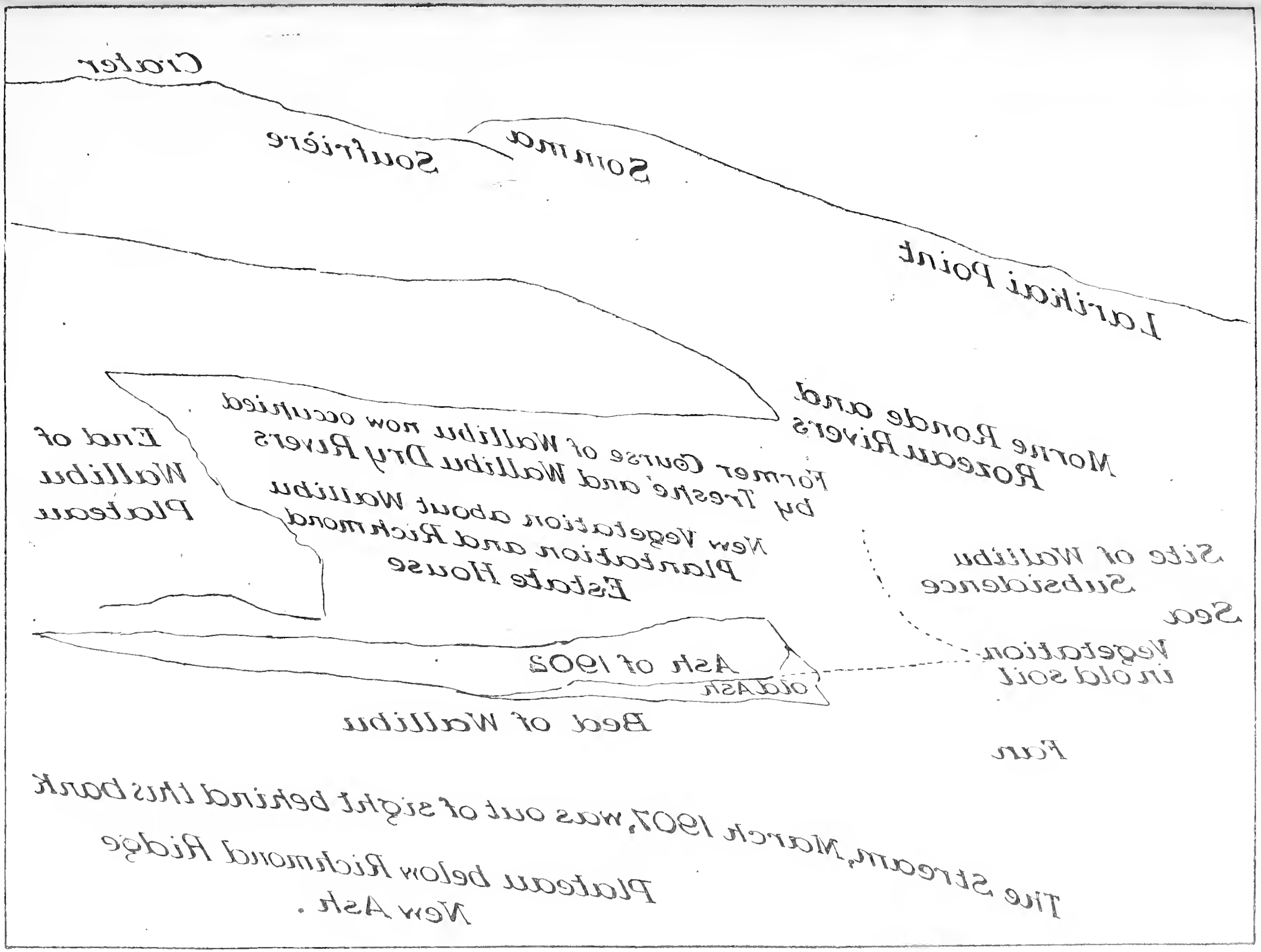

Ridges and Ravines
on slopes of Morne Garu.
Vegetation returning in old soil
now washed clear of fresh ash
Land
Slide
New Ravine
Tree Killed by Eruption
Incandescent Avalanche (1902)
surface channelled with Rain Rills
and consolidated into a crust.
Compare Part I. plate 26 which shews
early stage of such new
Ravines
Slope of
Soufrière,
Vegetation
returning
New Ravine

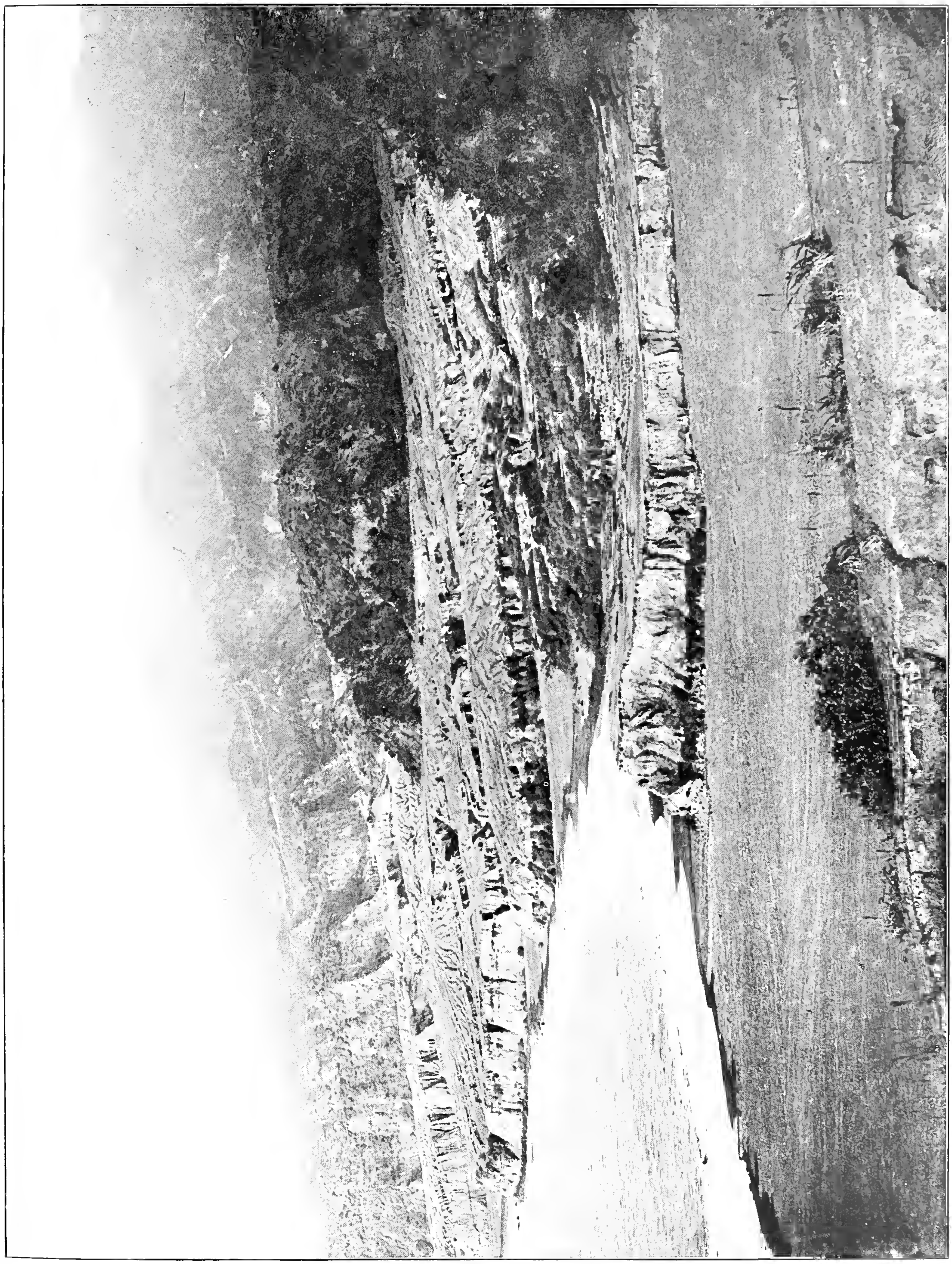
Ravine on Soufrière, Upper Trespé Valley.



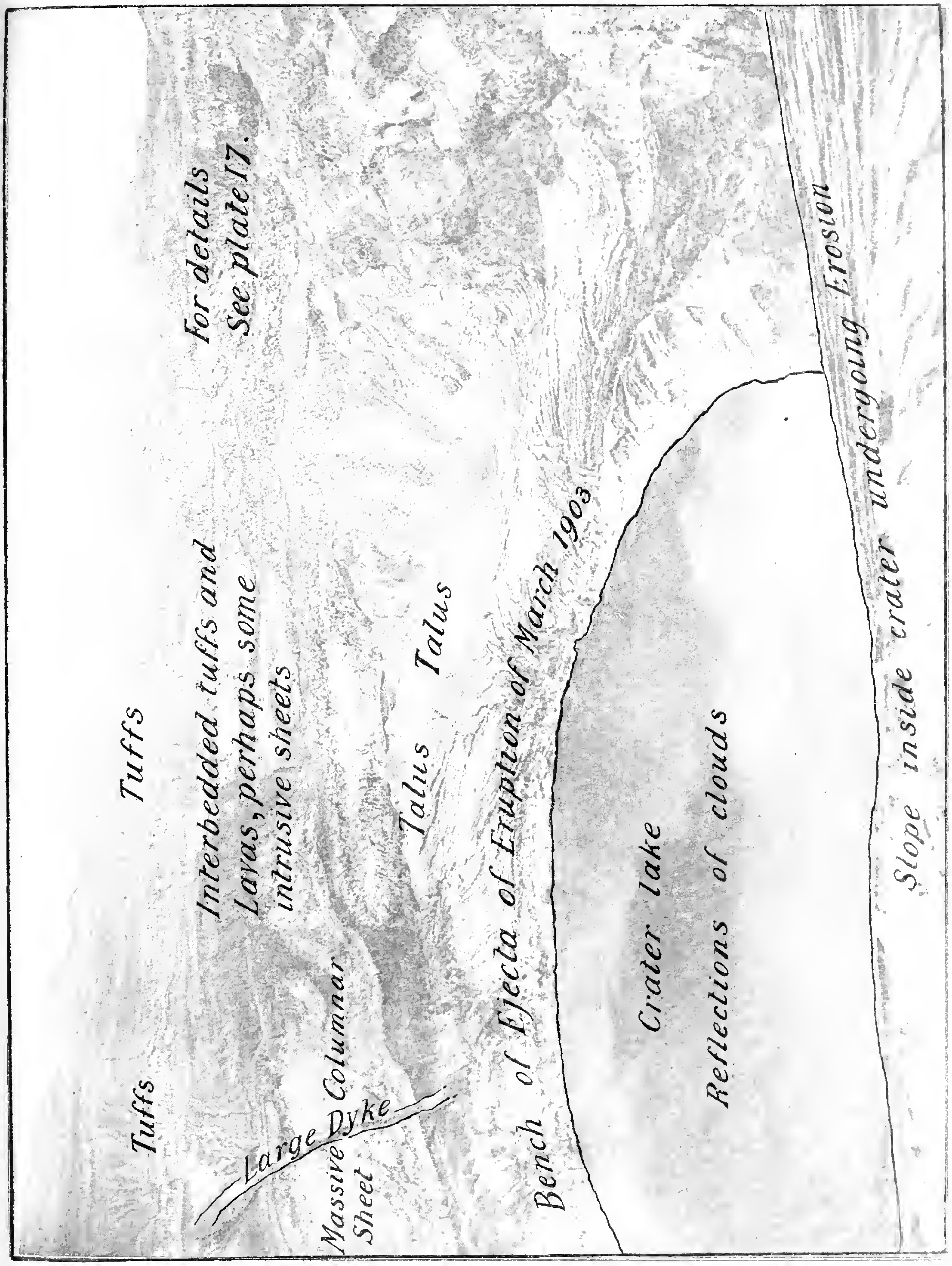
Mouth of Wallibu from Plateau below Richmond Ridge.


Crater
Somma
Soufrière
Larikai Point
Morne Ronde and Rozeau Rivers
Former Course of Wallibu now occupied by Treste' and Wallibu Dry Rivers
End of Wallibu Plateau
New Vegetation about Wallibu Plantation and Richmond Estate House
Site of Wallibu Subsidence
Sea
Vegetation in old soil
Ash of 1902
old Ash
Bed of Wallibu
Fan
The Stream, March 1907, was out of sight behind this bank
Plateau below Richmond Ridge
New Ash.

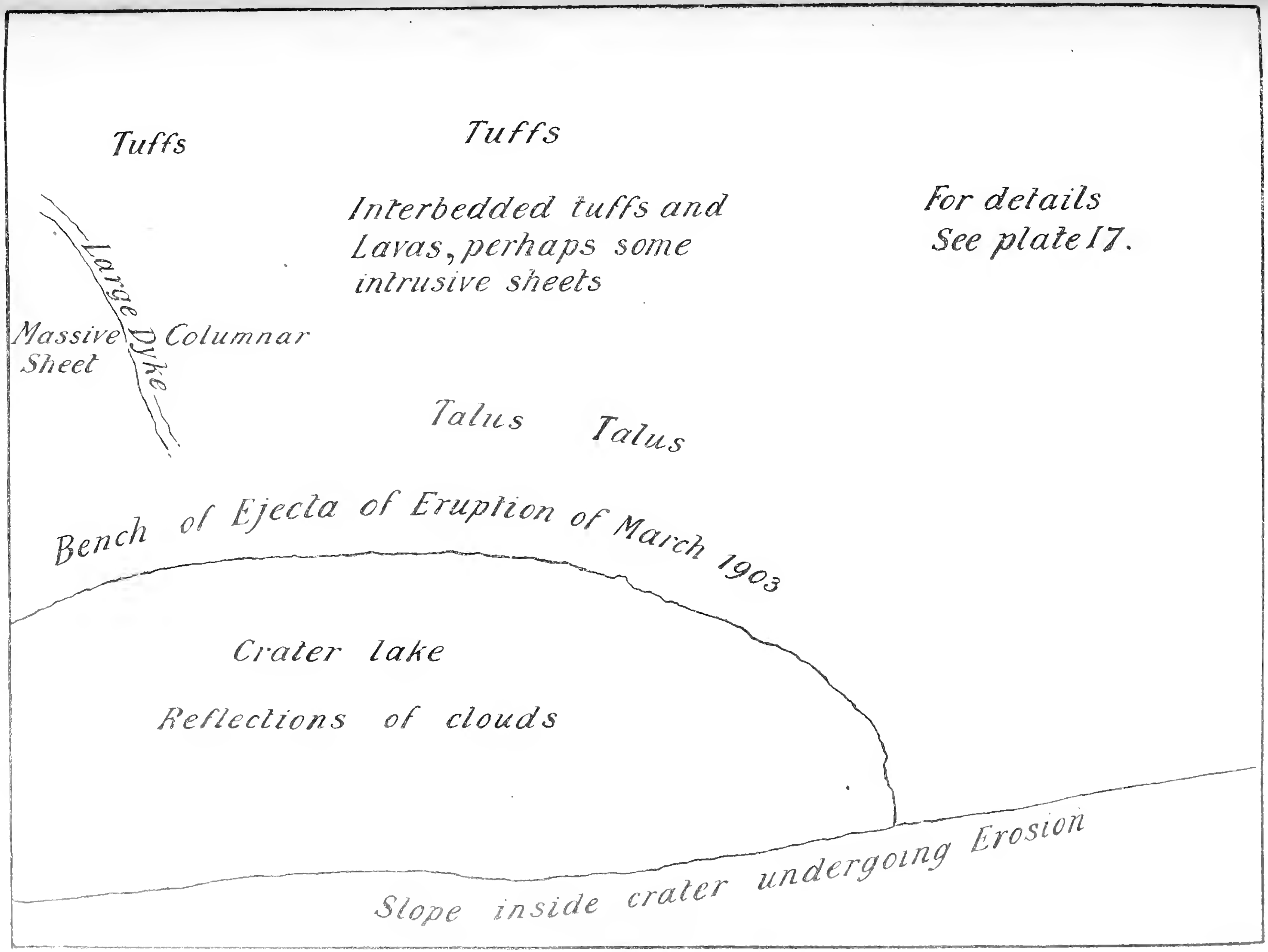

Crater
Soufrière
Somma
Larikai Point
Morne Ronde and Rozeau Rivers
End of Wallibu Plateau
Former Course of Wallibu now occupied by TresHe and Wallibu Dry Rivers
New Vegetation about Wallibu Plantation and Richmond Estate House
Site of Wallibu Subsidence
Sea
Vegetation in old soil
Ash of 1902
old Ash
Bed of Wallibu
Fern
The Stream, March 1907, was out of sight behind this bank
Plateau below Richmond Ridge
New Ash.

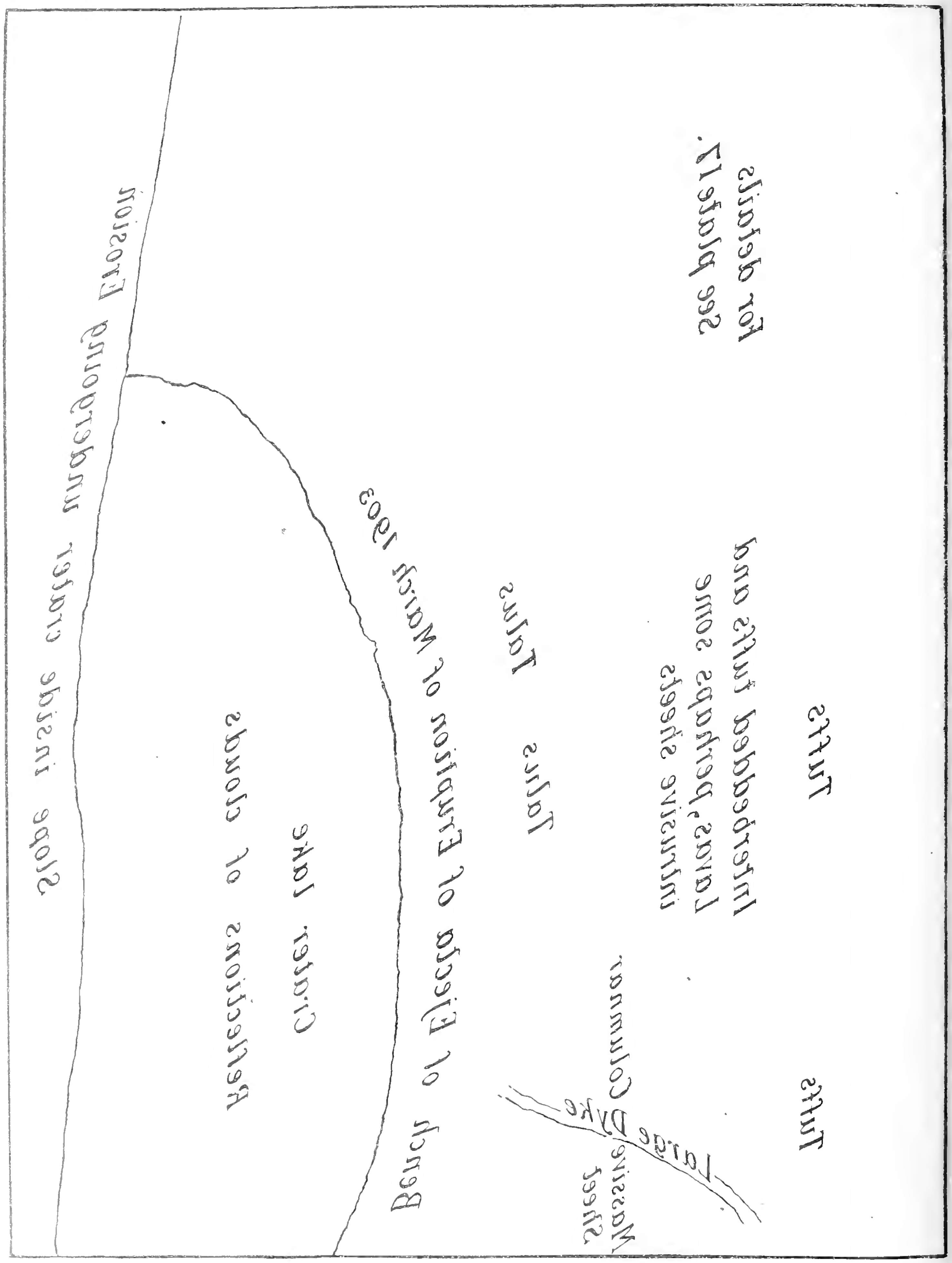


Mouth of Wallibu, from Plateau below Richmond Ridge.

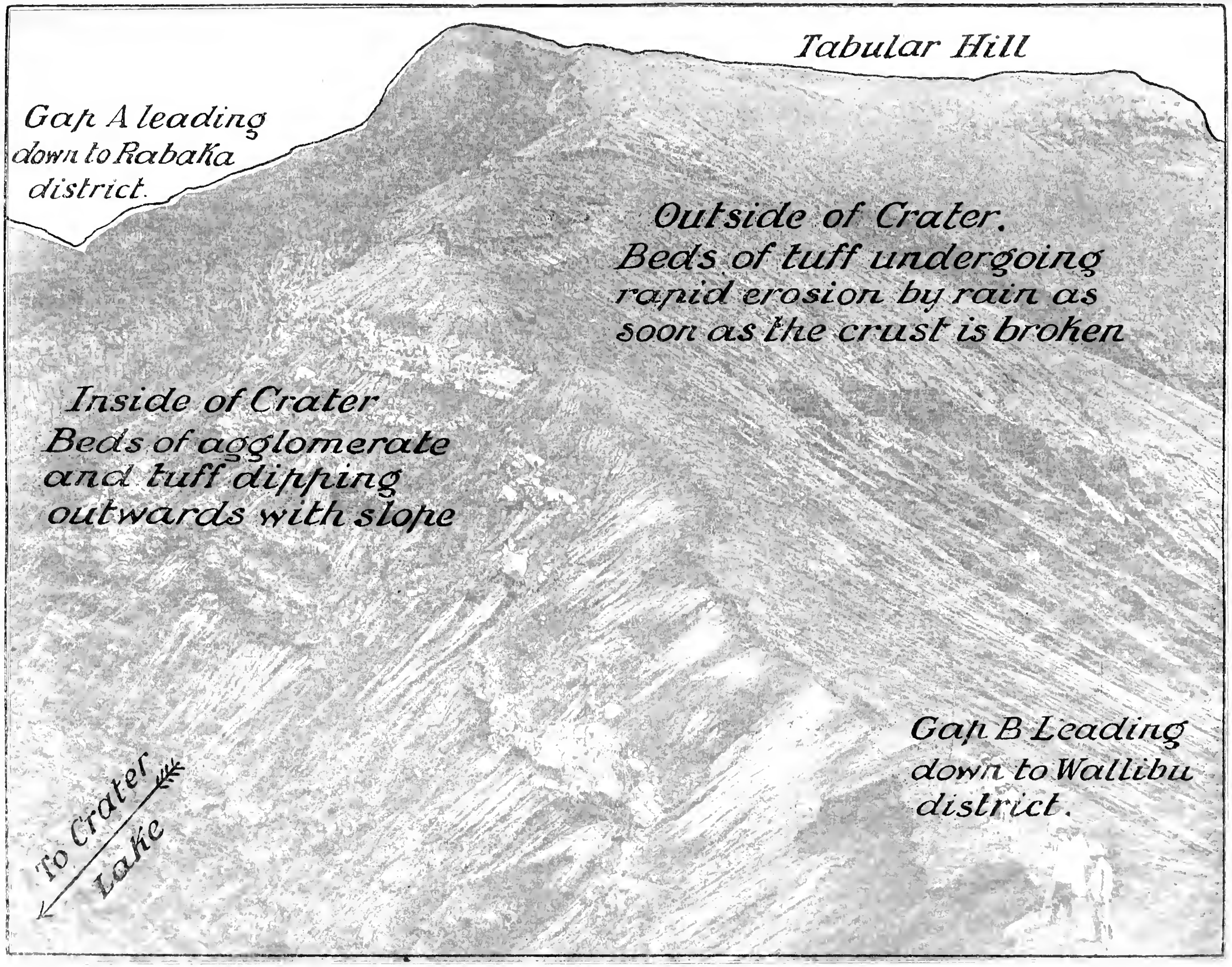


The Crater of the Soufrière from the South in

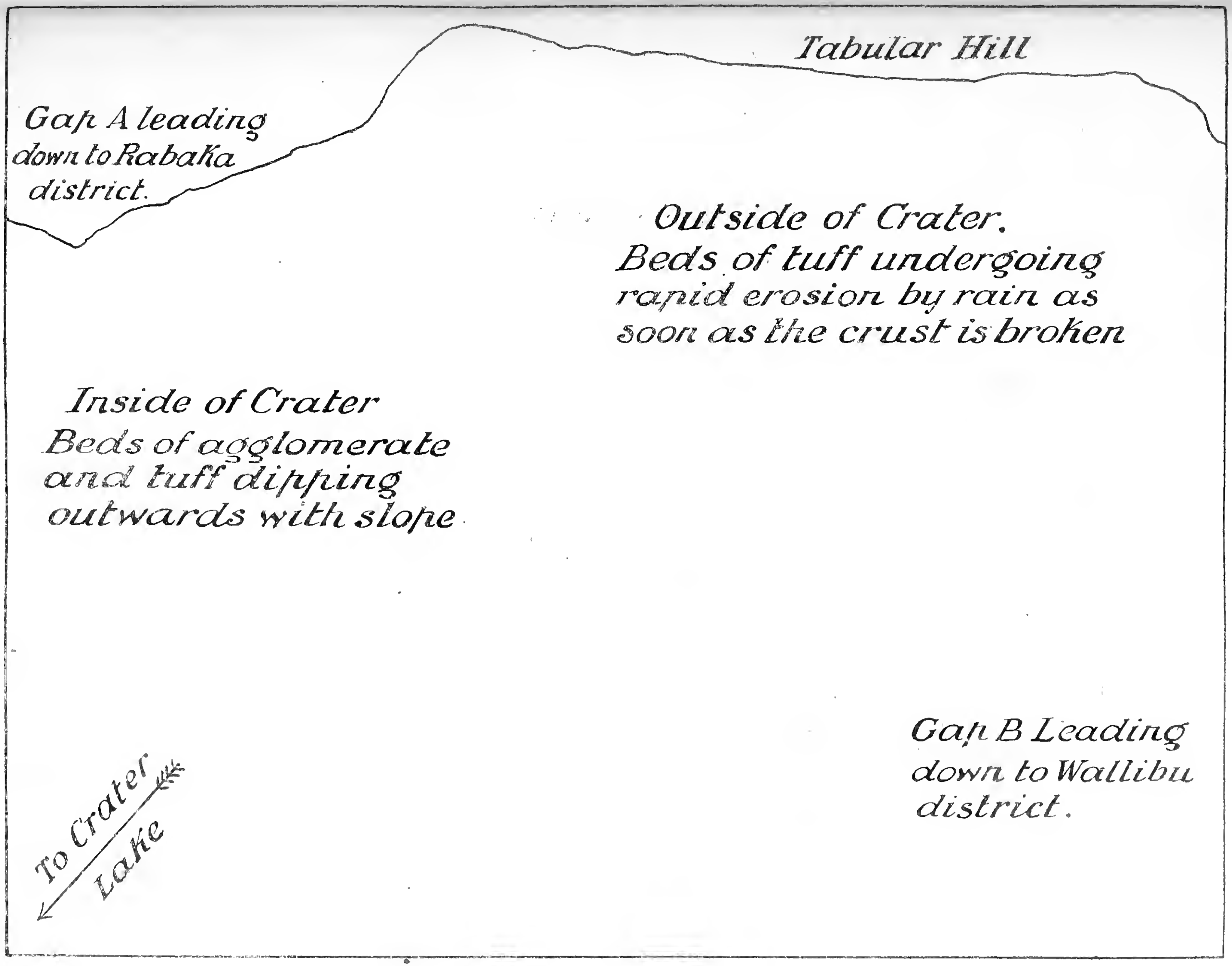

Tuffs
Tuffs
Interbedded tuffs and Lavas, perhaps some intrusive sheets
For details See plate 17.
Large Dyke
Massive Sheet
Columnar
Talus
Talus
Bench of Ejecta of Eruption of March 1903
Crater lake
Reflections of clouds
Slope inside crater undergoing Erosion


Tuffs
Tuffs
For details
See plate 17.
Interbedded tuffs and
Lavas, perhaps some
intrusive sheets
Massive Columnar
Sheet
Large Dyke
Talus
Talus
Bench of Ejecta of Eruption of March 1903
Crater lake
Reflections of clouds
Slope inside crater undergoing Erosion

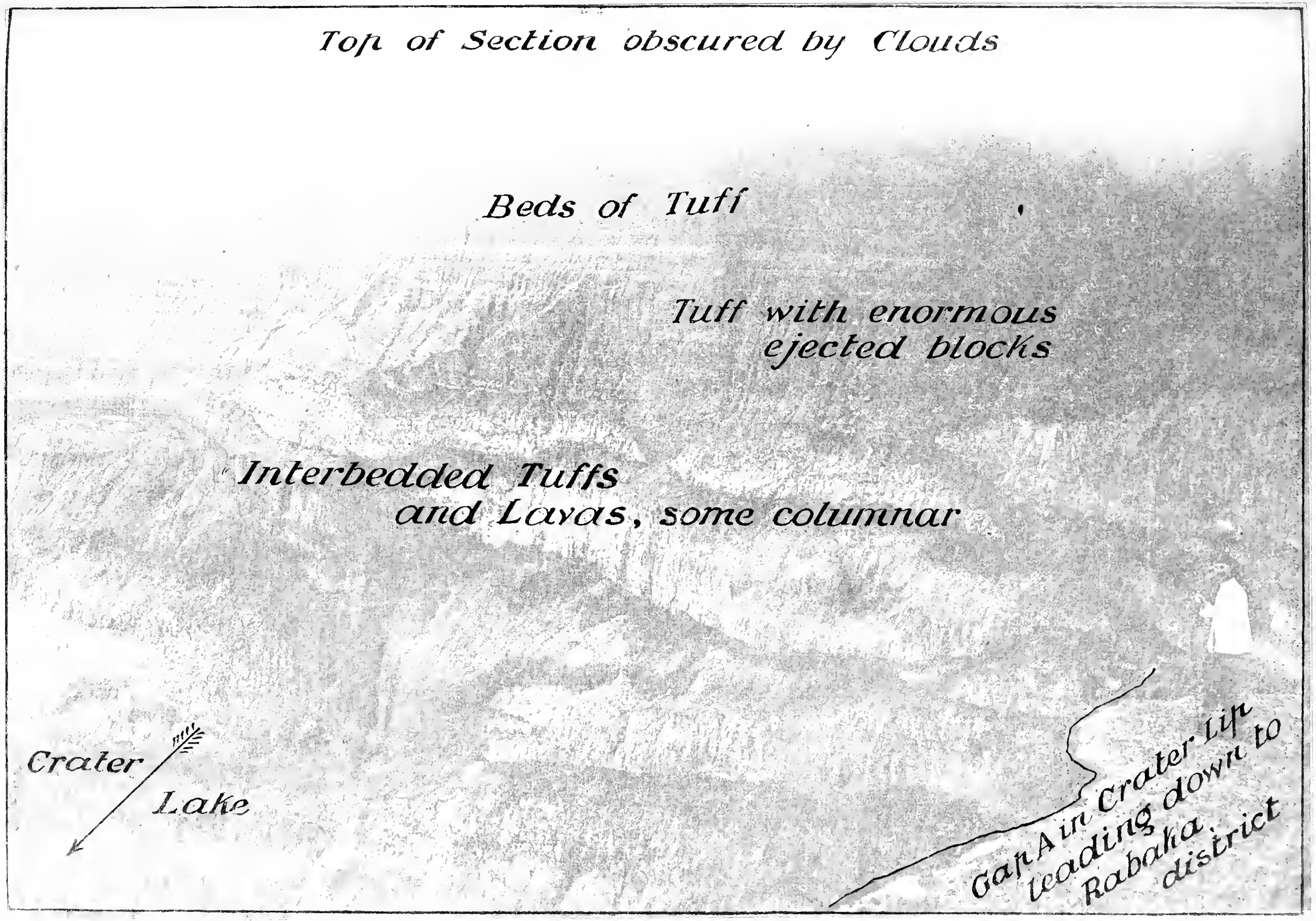
The Crater of the Soufrière, from the South-west lip.



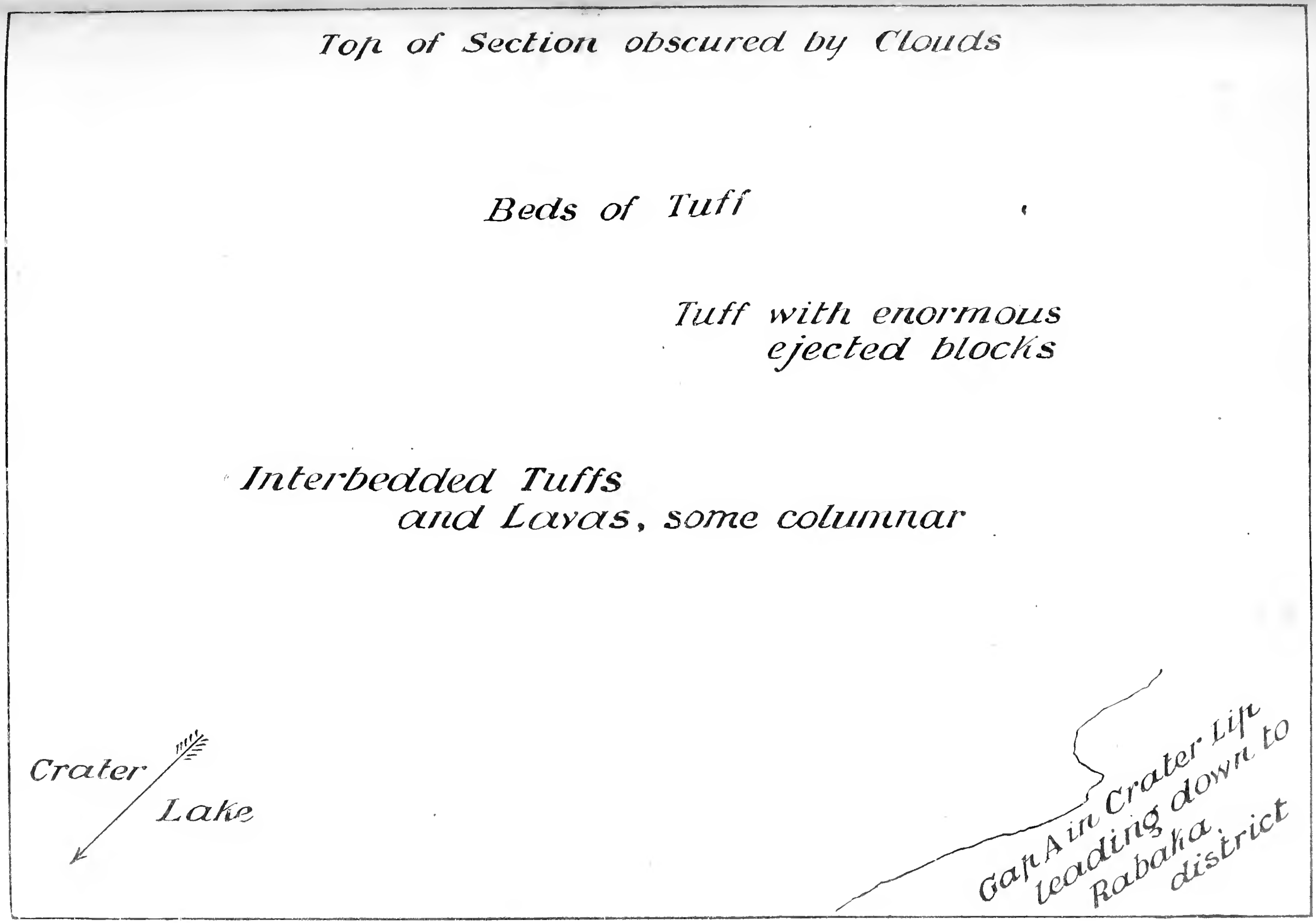
Crater of the Soufrière; south lip, from West.

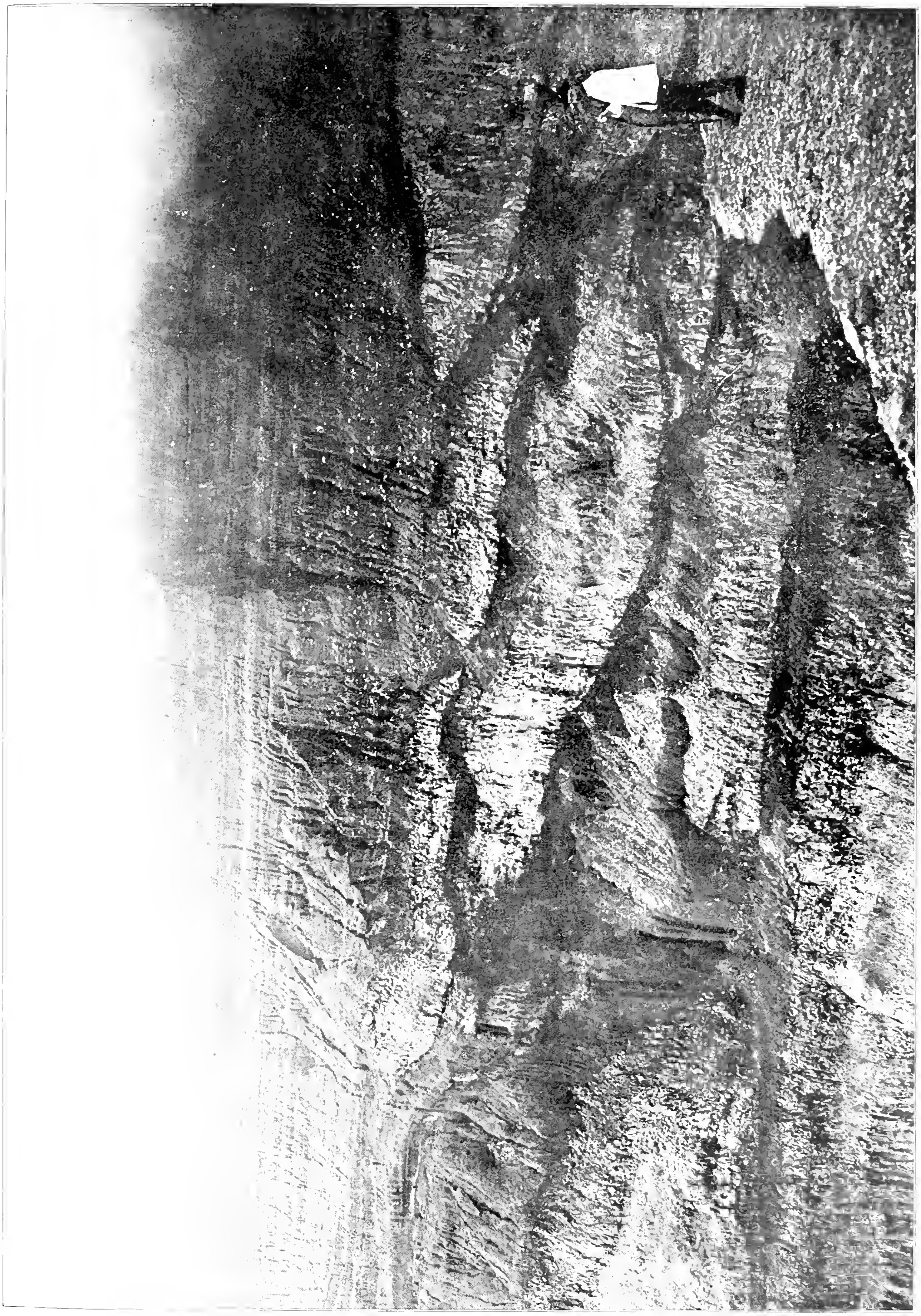

Tabular Hill
Gap A leading
down to Rabaka
district.
Outside of Crater.
Beds of tuff undergoing
rapid erosion by rain as
soon as the crust is broken
Inside of Crater
Beds of agglomerate
and tuff dipping
outwards with slope
Gap B Leading
down to Wallibu
district.
To Crater
Lake

Crater of the Soufrière; south lip, from West.

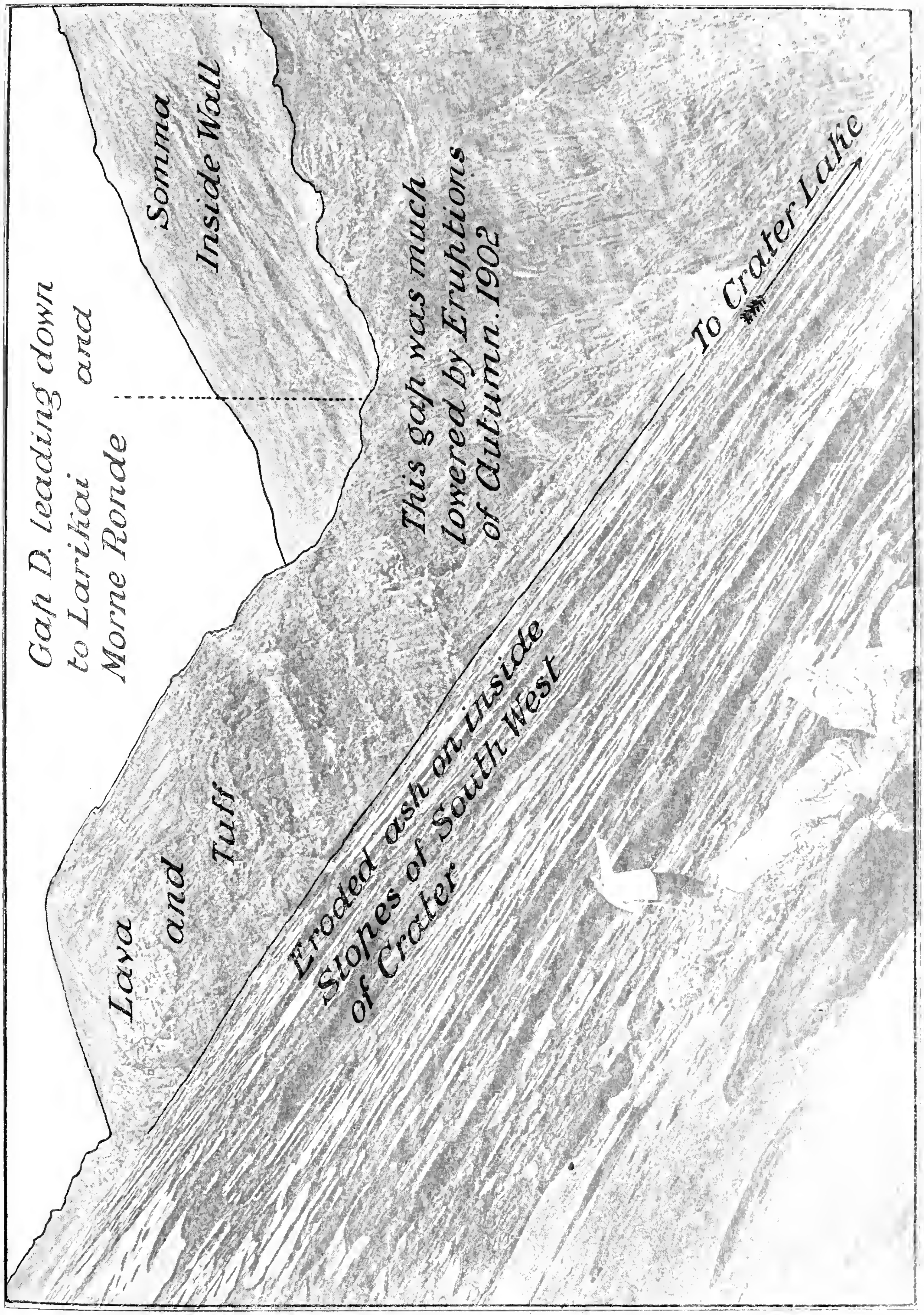


North wall of Crater, Eastern end.

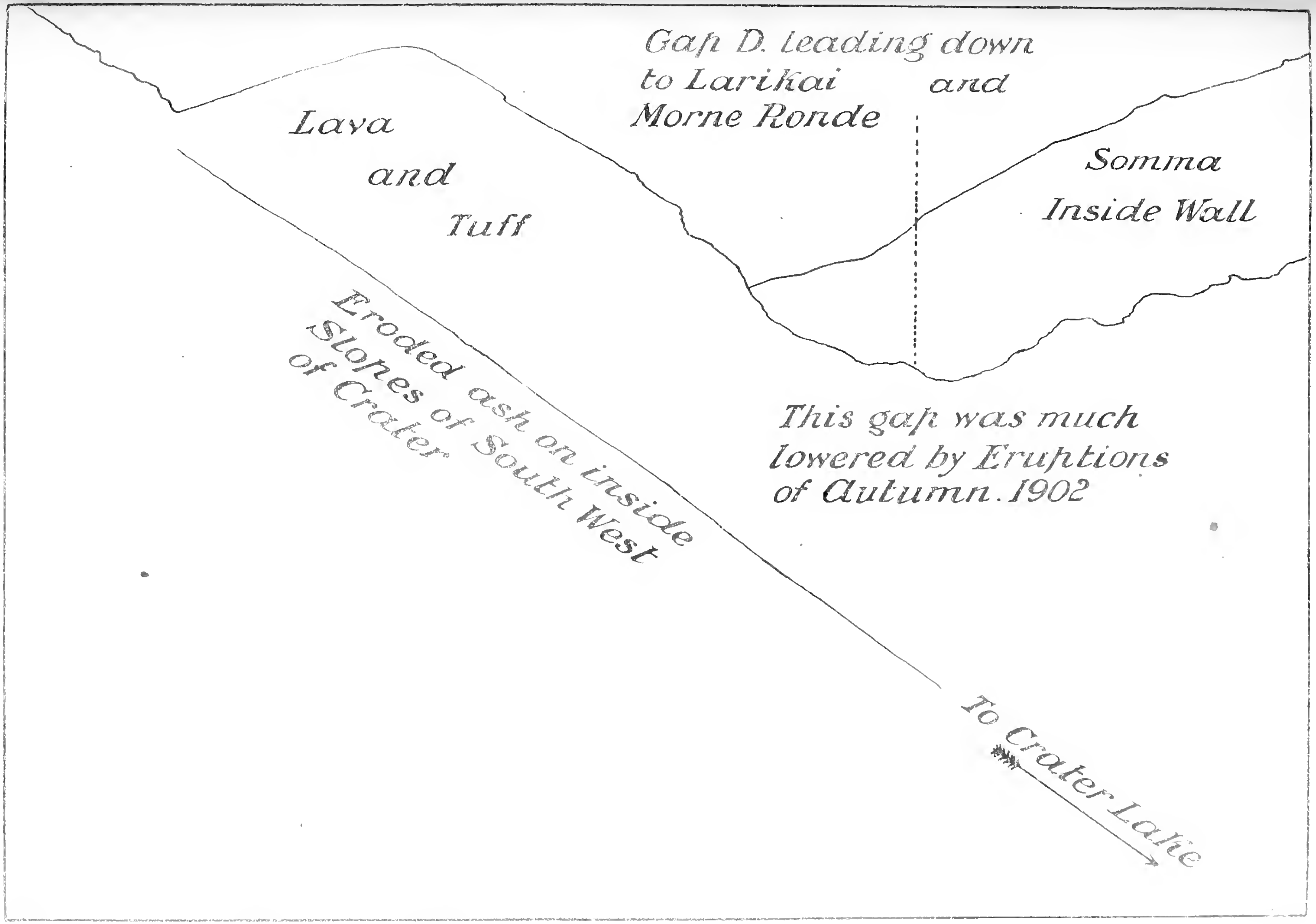

Top of Section obscured by Clouds
Beds of Tuff
Tuff with enormous ejected blocks
Interbedded Tuffs and Lavas, some columnar
Crater Lake
Gap A in Crater Lip leading down to Rabaka district

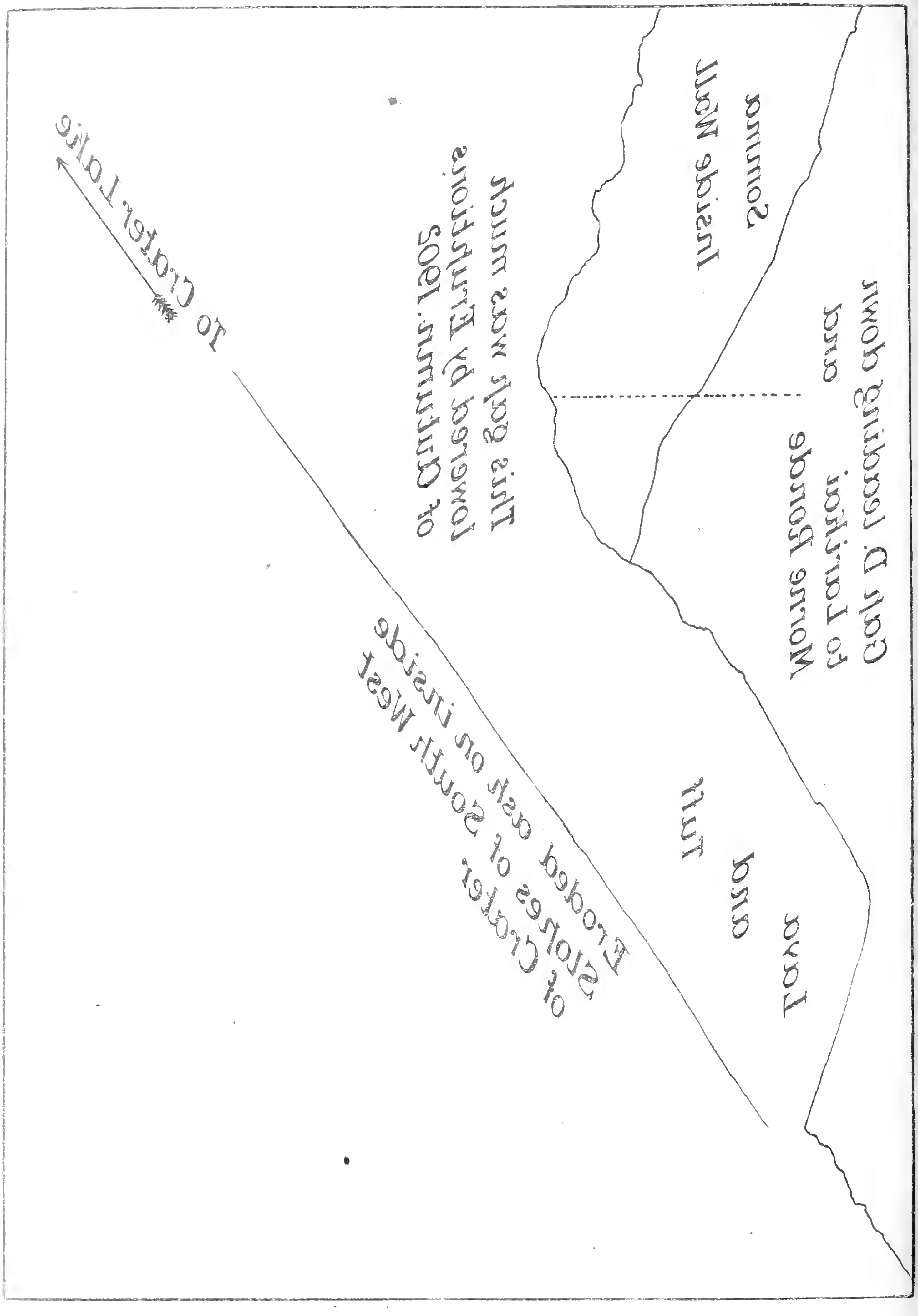


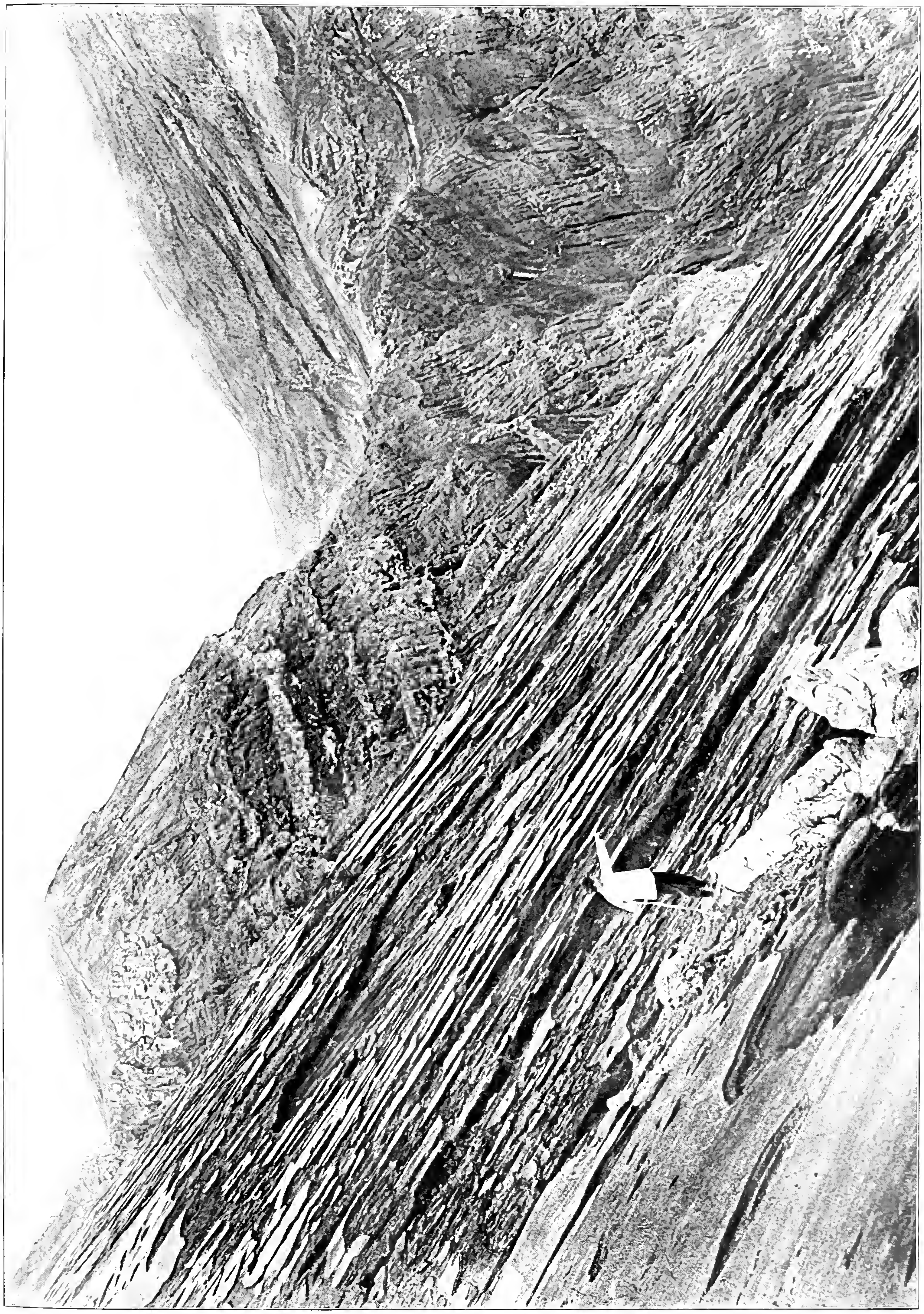
North wall of Crater, Eastern end



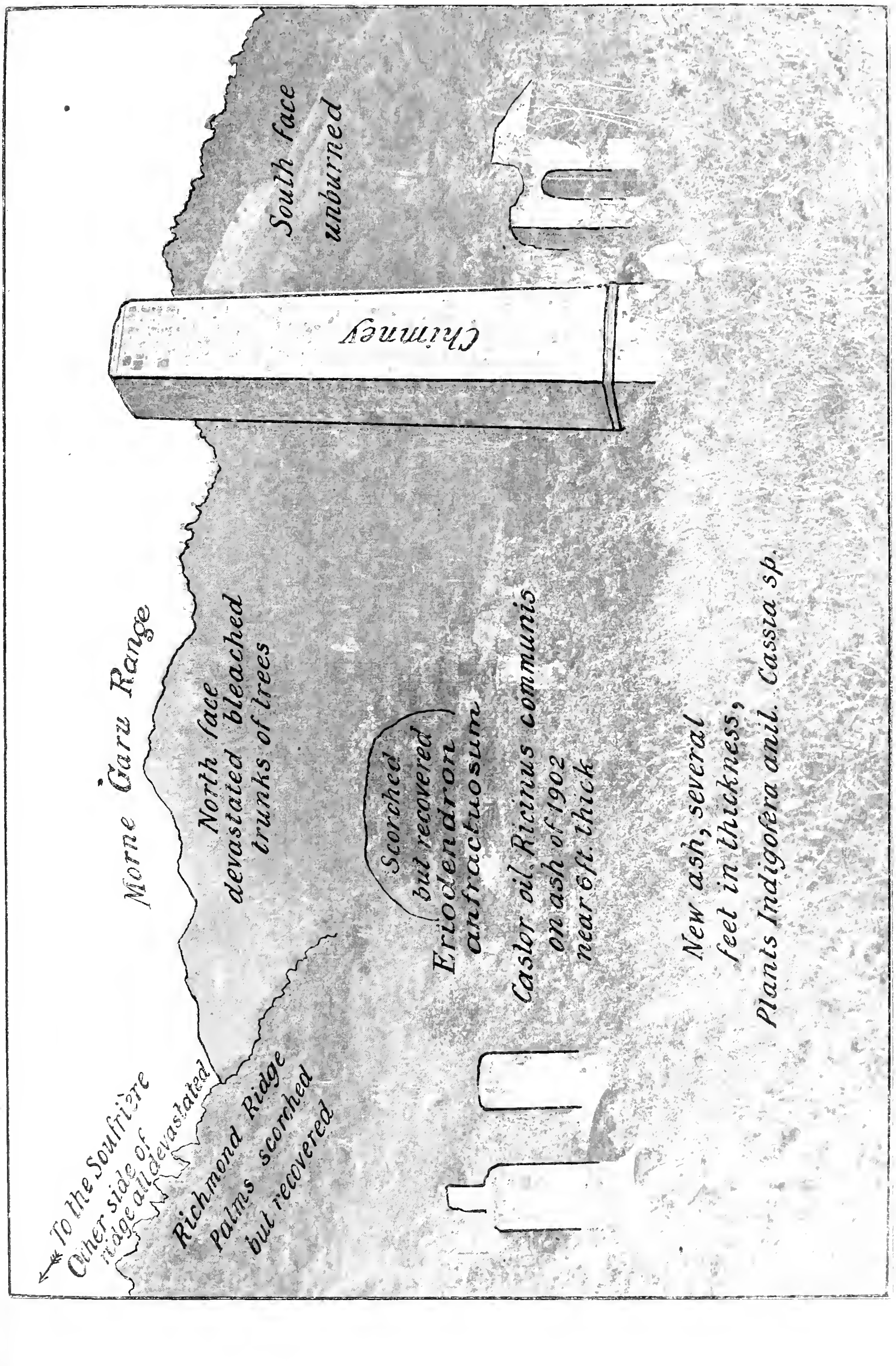
West Lip of Crater.


Gap D. leading down to Larikai and Morne Ronde
Lava and Tuff
Somma Inside Wall
This gap was much lowered by Eruptions of Autumn. 1902
Eroded ash on inside Slopes of South West of Crater
To Crater Lake

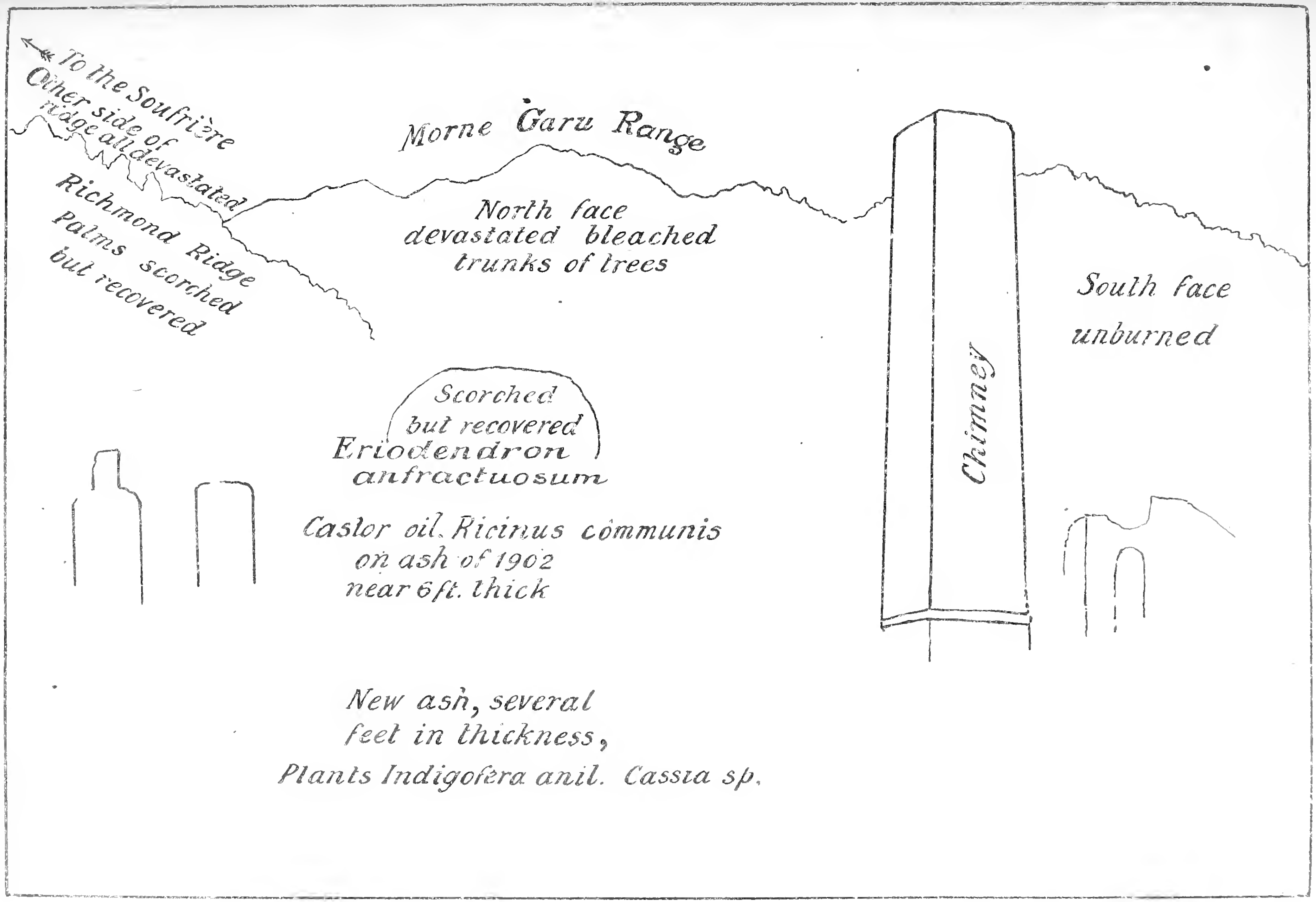

To Crater Lake
This gap was much lowered by Eruptions of Autumn 1902
Inside Wall Somma
Gap D leading down to Larikai and Morne Ronde
Lava and Tuff
Eroded ash on inside slopes of South West of Crater

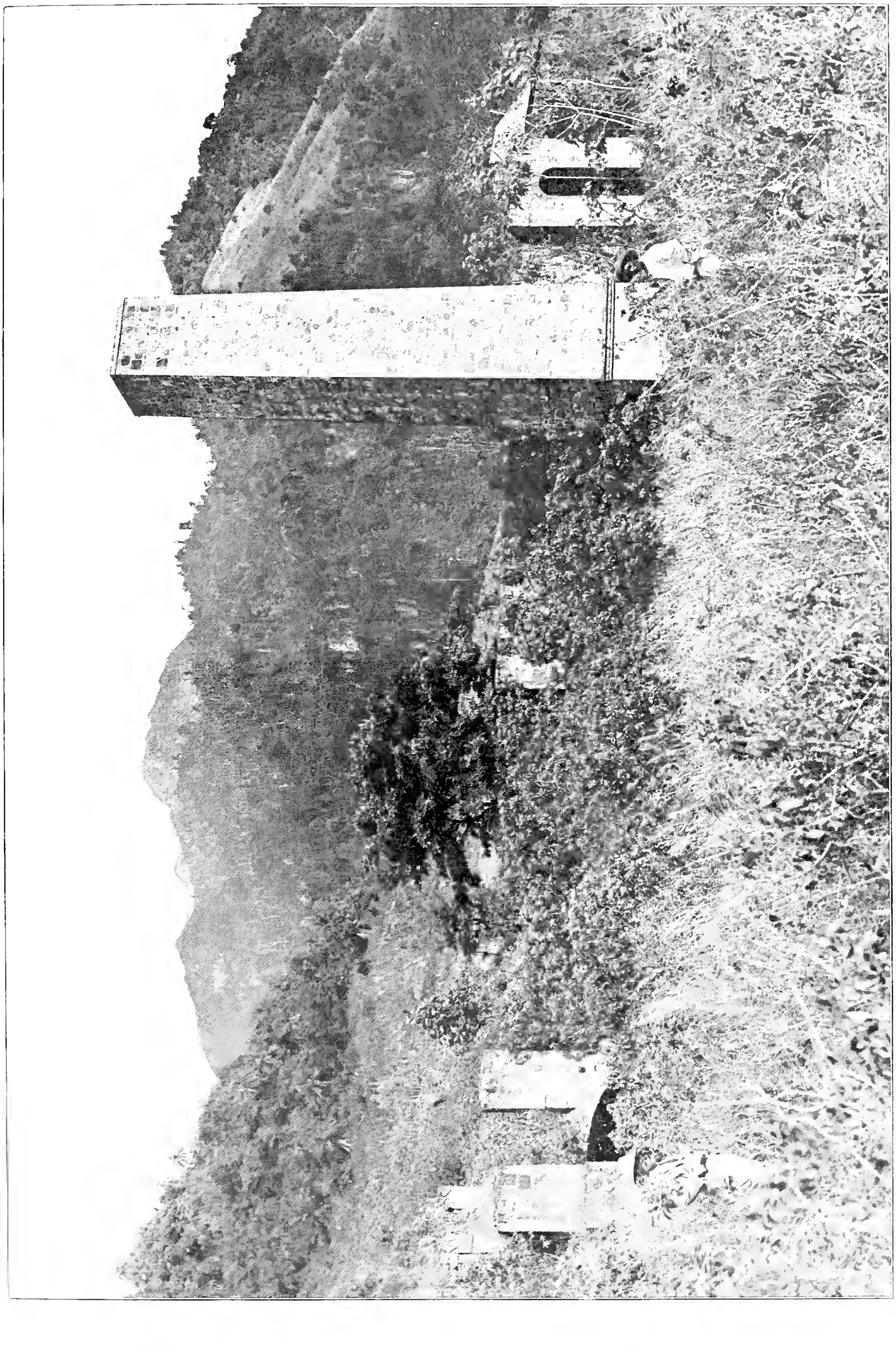


West lip of Crater.



Richmond Plantation Works, 1907, from the West.


To the Soufrière
Other side of ridge all devastated
Morne Garu Range
North face devastated bleached trunks of trees
Richmond Ridge
Palms scorched but recovered
South face unburned
Chimney
Scorched but recovered
Eriodendron anfractuosum
Castor oil. Ricinus communis on ash of 1902 near 6ft. thick
New ash, several feet in thickness,
Plants Indigofera anil. Cassia sp.



Richmond Plantation Works, 1907, from the West.

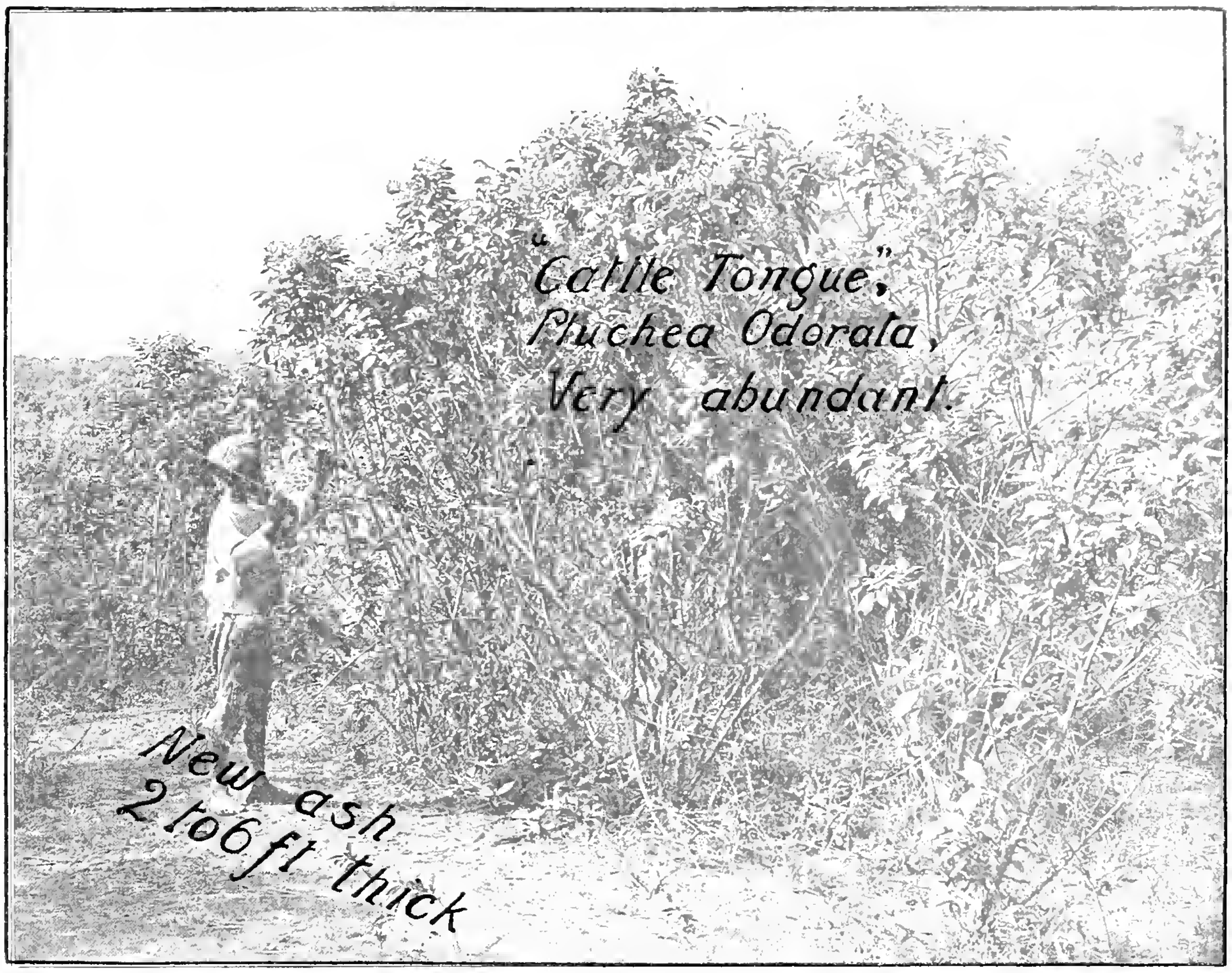


Fig. 1. *Near Richmond Works* 1907. (Pluchea Odorata.)

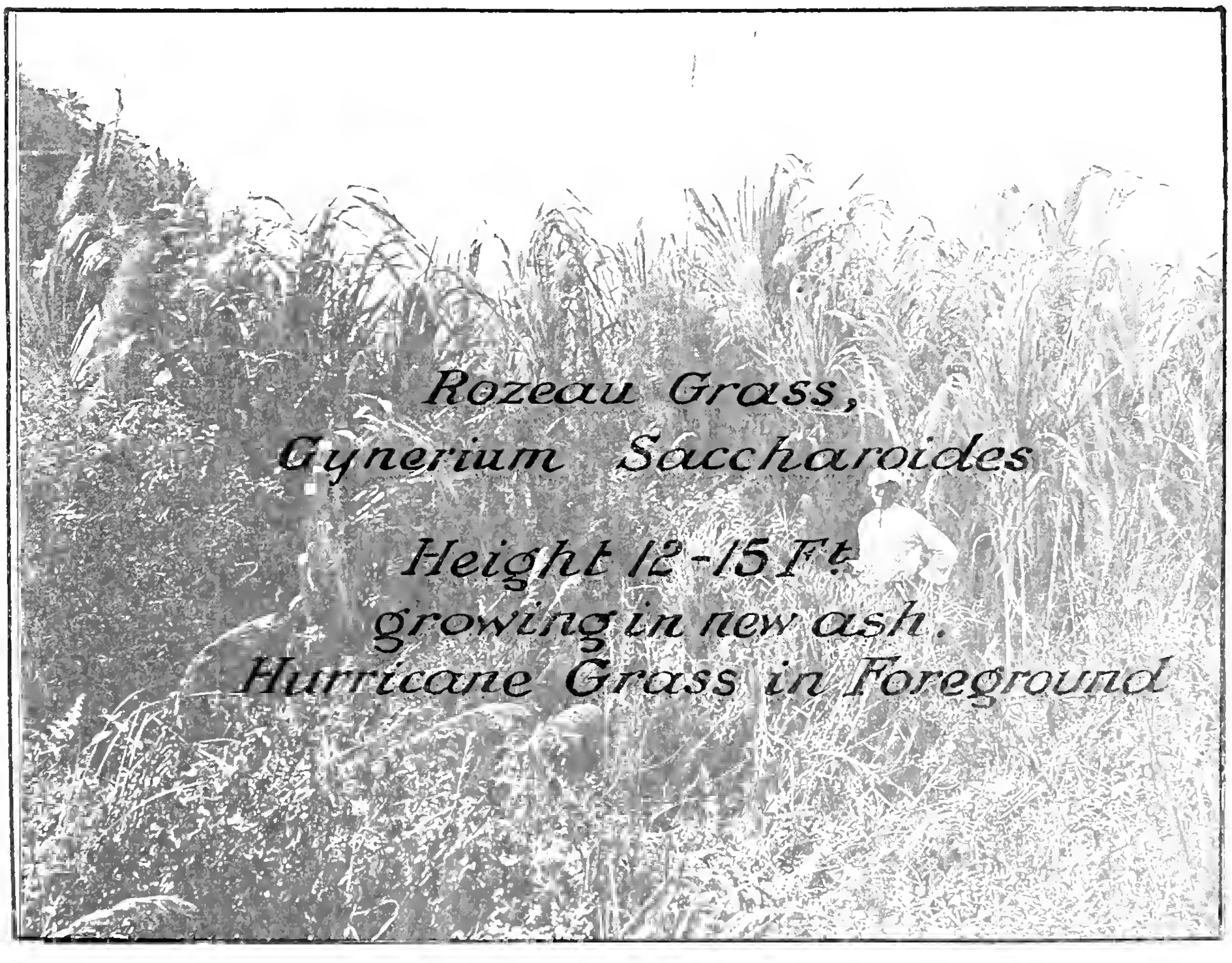


Fig. 2. *Near the River, Richmond Works.*

"Cattle Tongue",
Pluchea Odorata,
Very abundant.

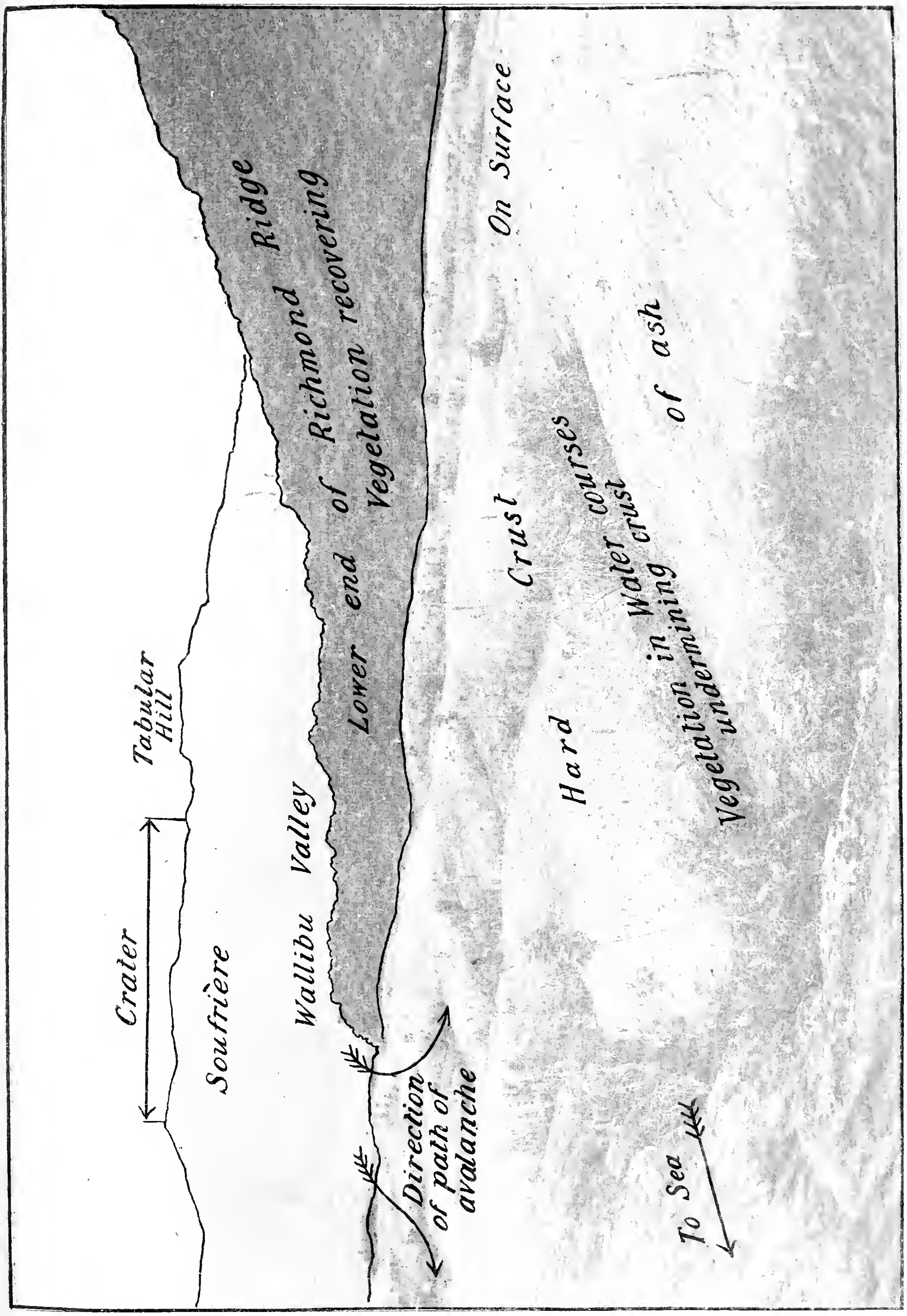
New ash
2 to 6 ft thick

Rozeau Grass,
Gynerium Saccharoides

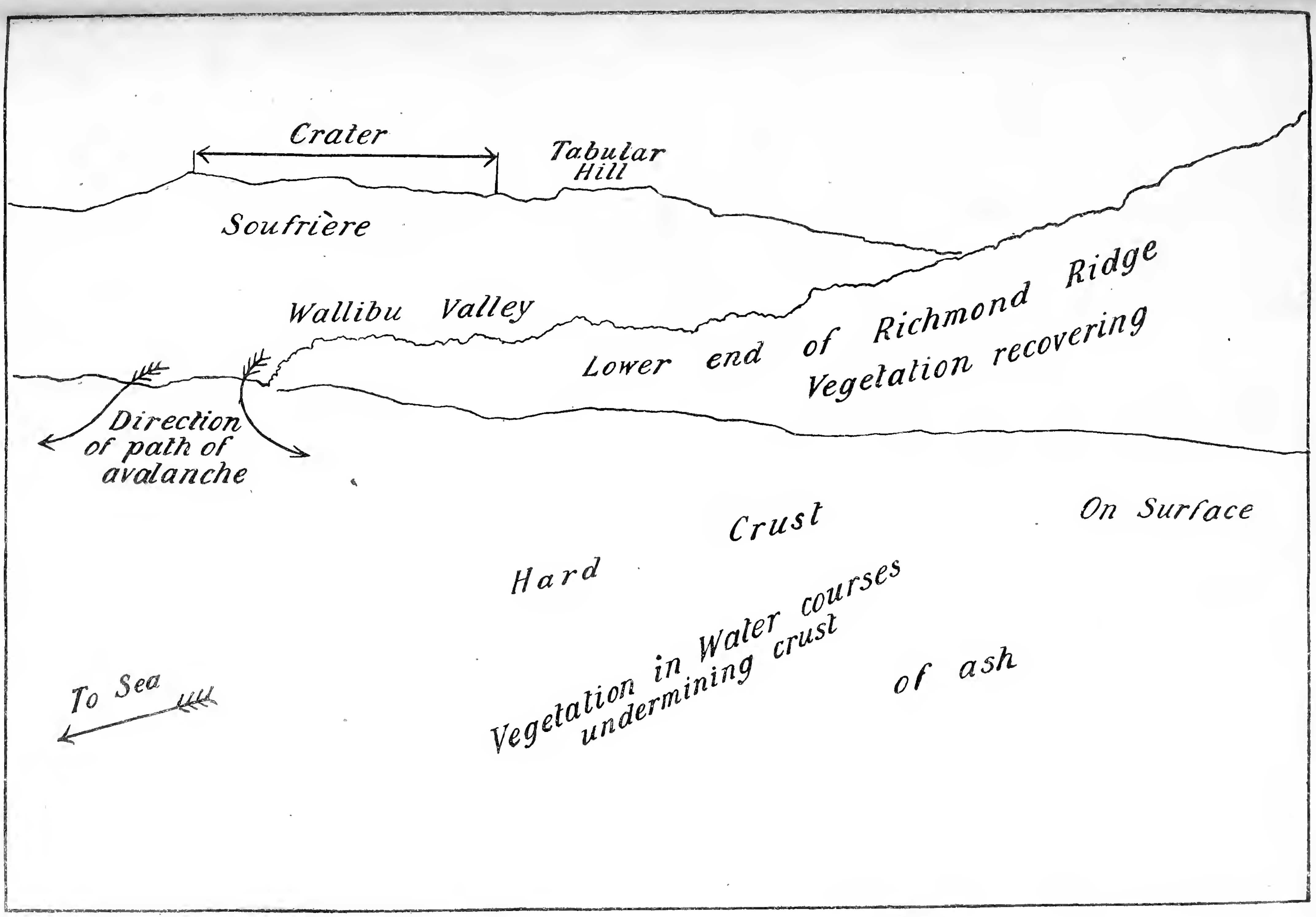
Height 12-15 Ft.
growing in new ash.
Hurricane Grass in Foreground

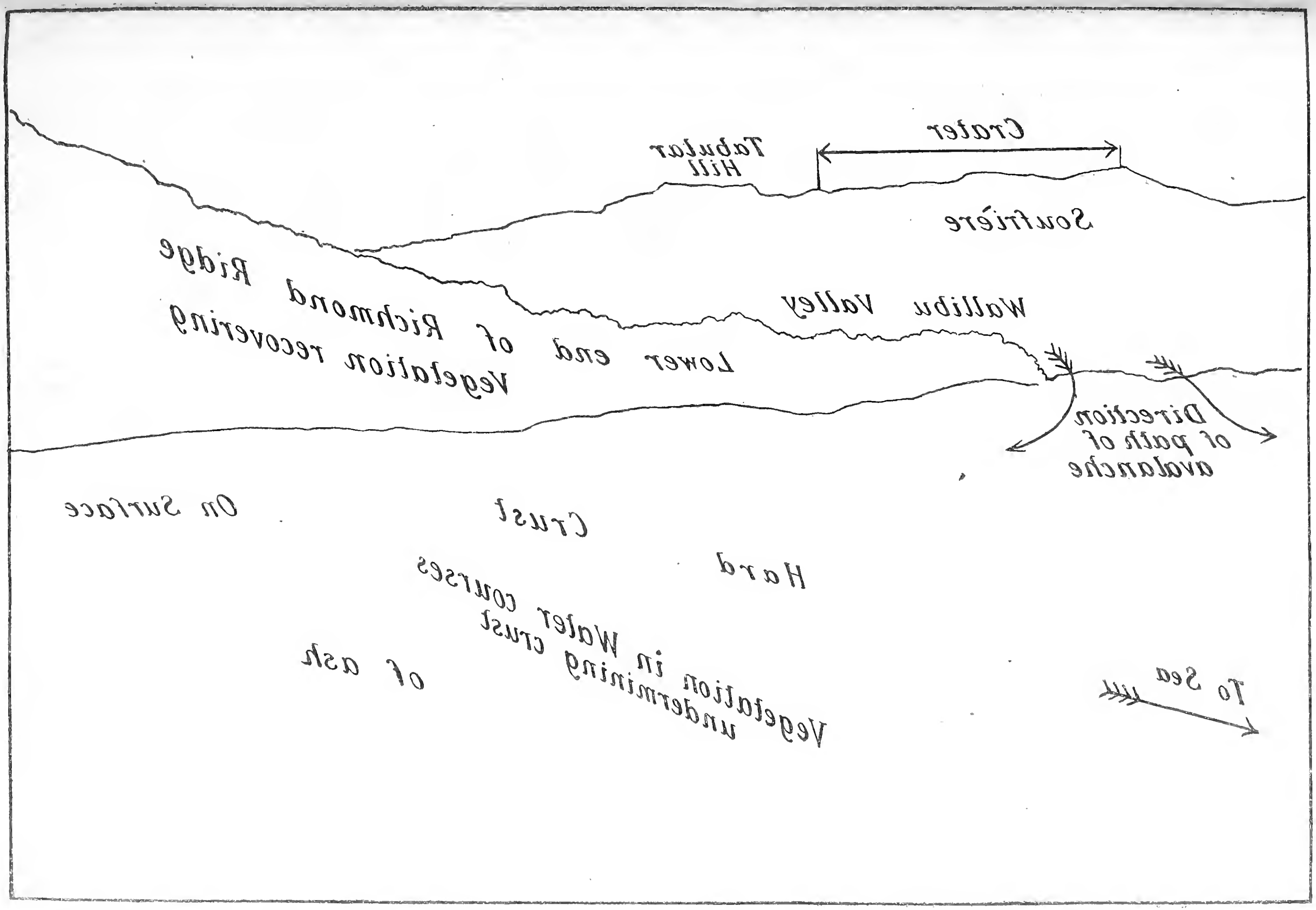
Fig. 1. *Near Richmond Works*, 1907. (Pluchea Odorata.)

Fig. 2. *Near the River, Richmond Works.*



The Avalanche, below end of Richmond Ridge.


Crater
Tabular Hill
Soufrière
Wallibu Valley
Lower end of Richmond Ridge
Vegetation recovering
Direction of path of avalanche
Hard Crust On Surface of ash
Vegetation in Water courses undermining crust
To Sea


Crater
Tabular Hill
Soufrière
Ridge
Lower end of Richmond
Vegetation recovering
Wallibu Valley
Direction of path of avalanche
On Surface
Hard Crust
Vegetation in Water courses undermining crust of ash
To Sea

The Avalanche, below end of Richmond Ridge.

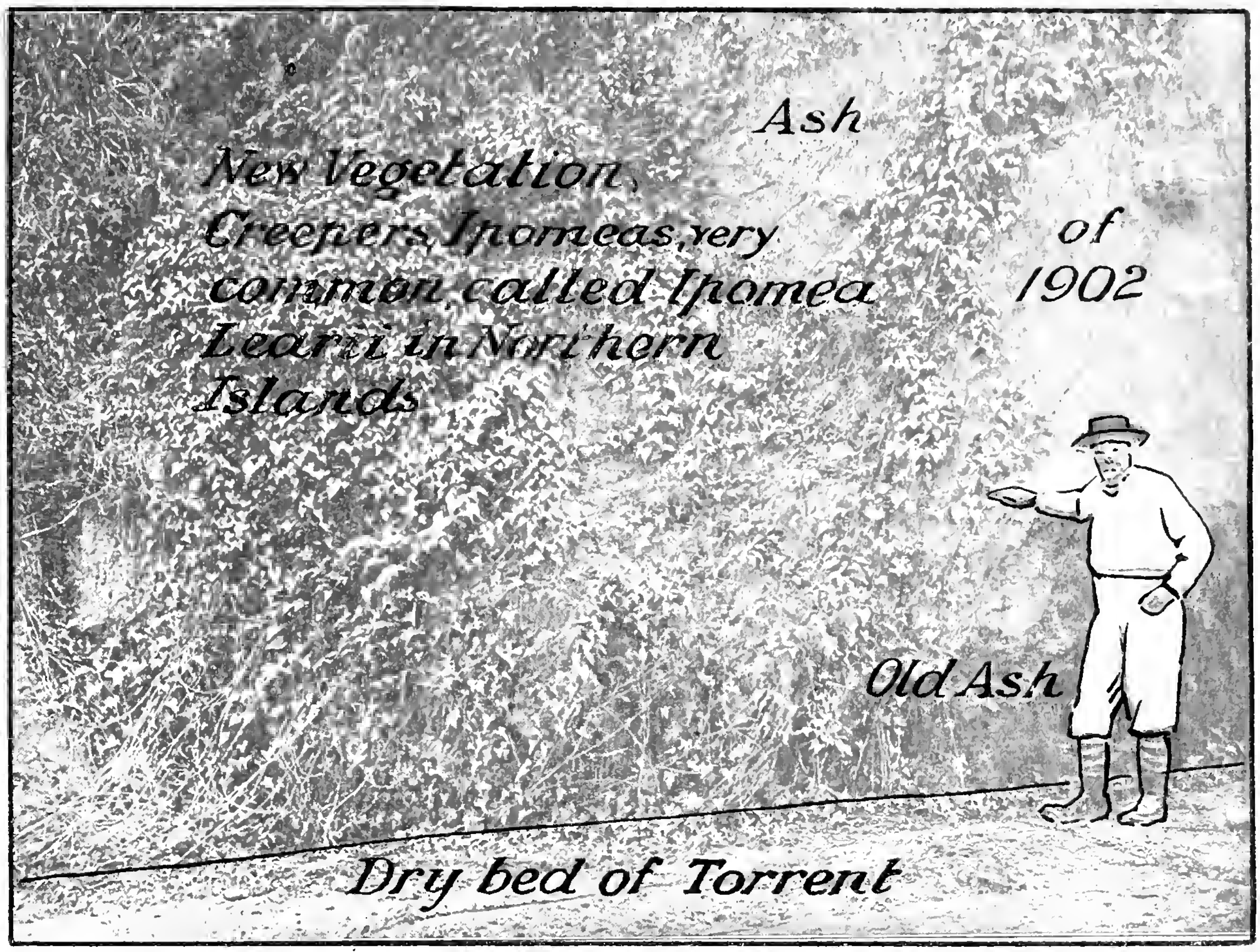


Fig. 1. *North Wall of Trespé Valley.*

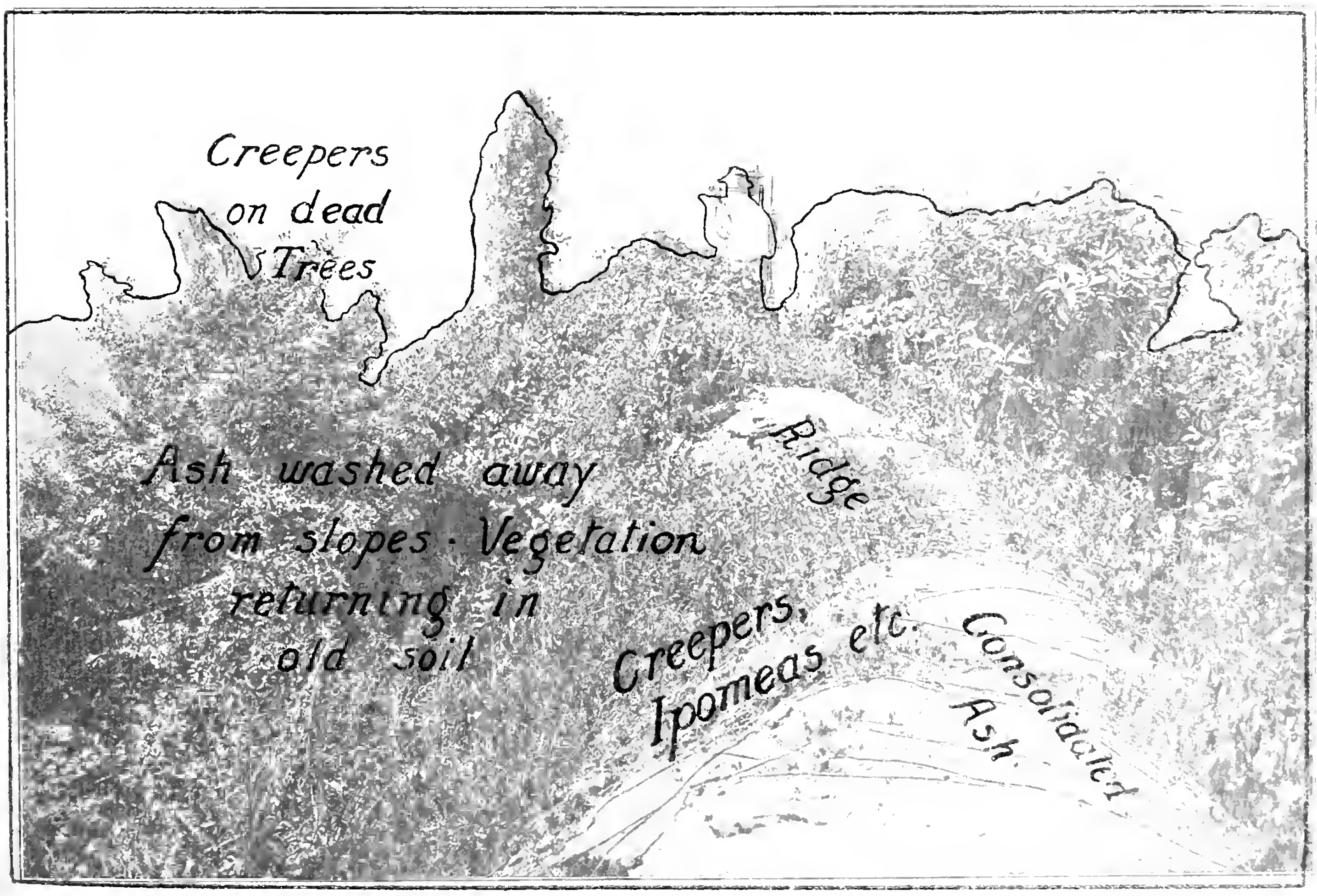
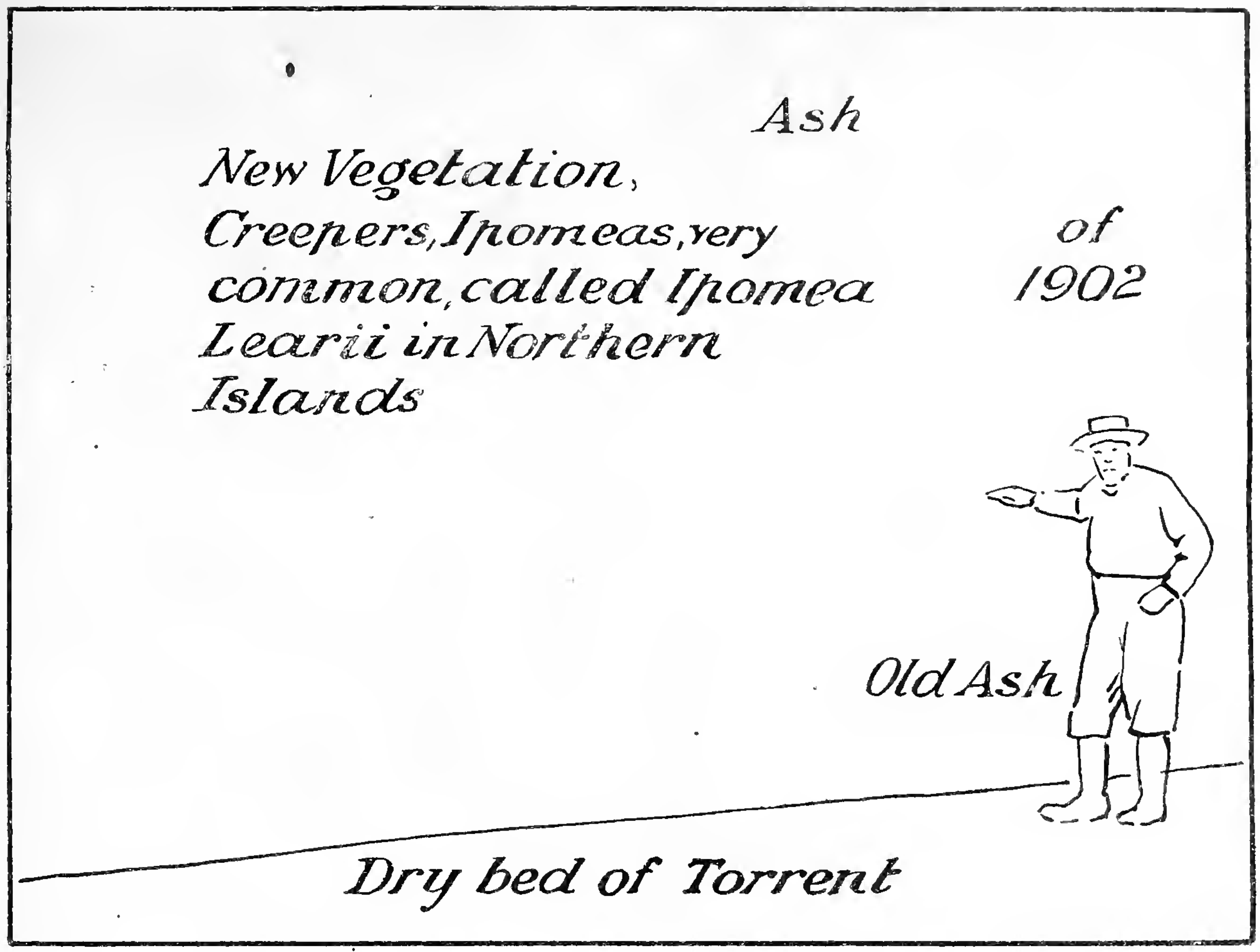
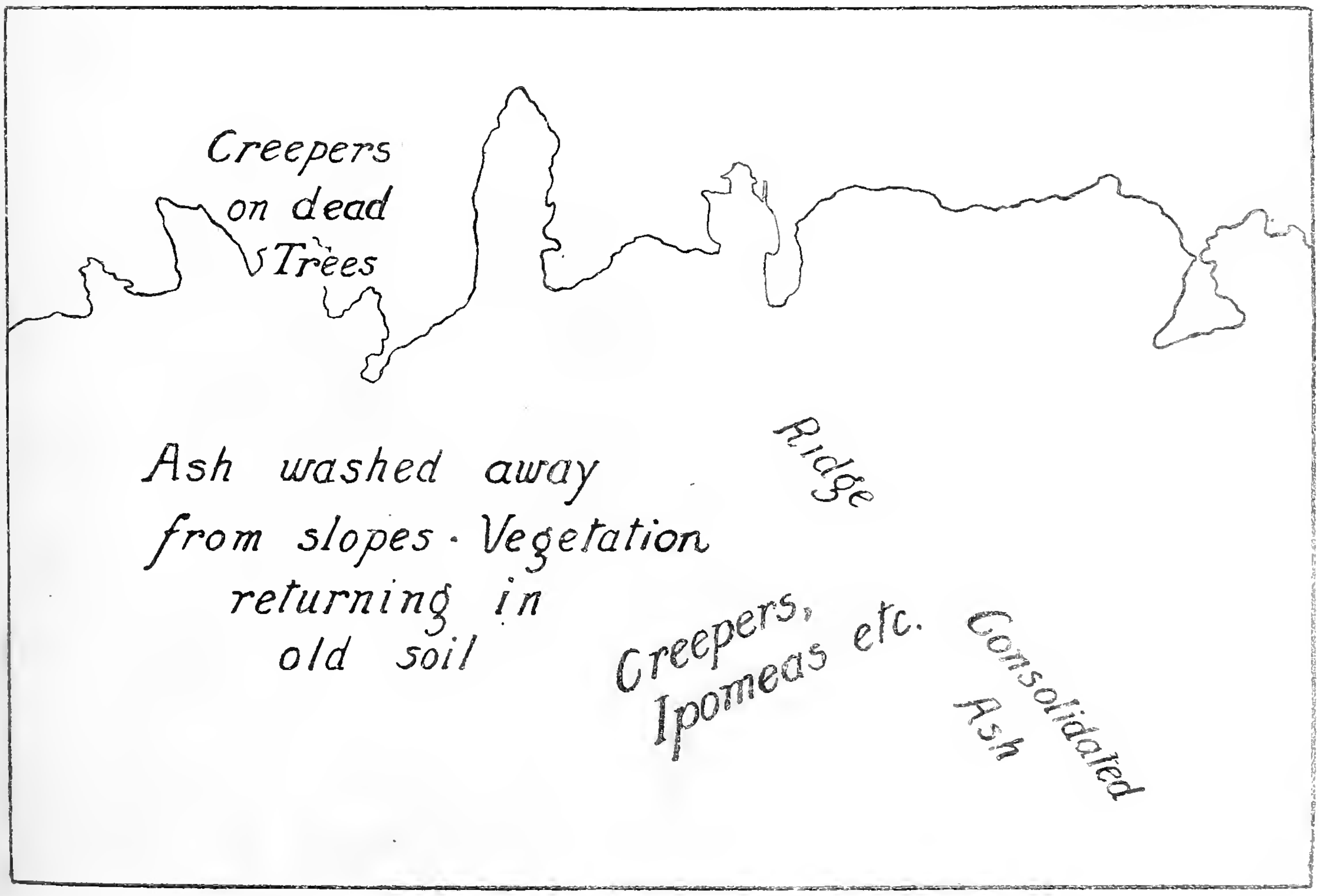
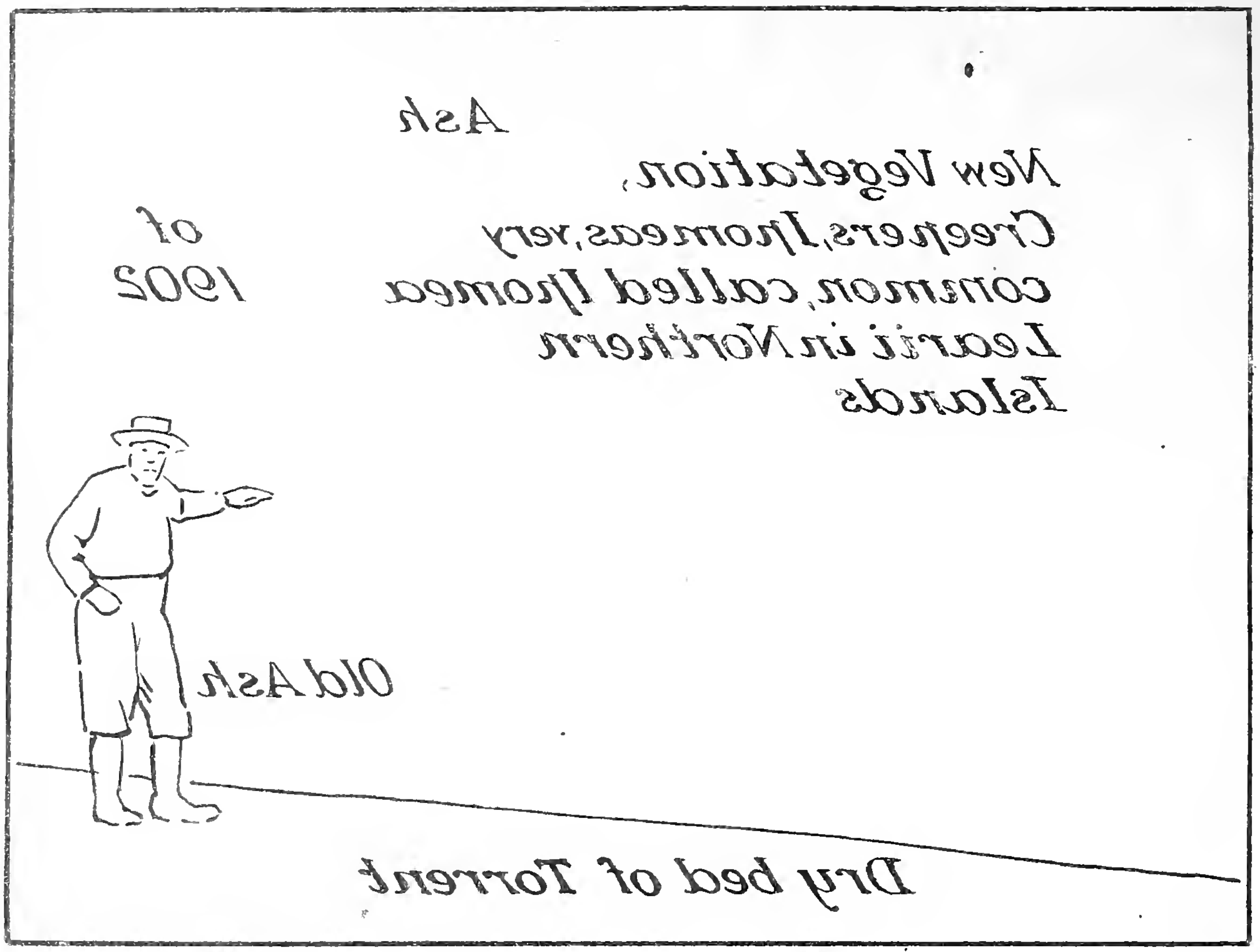


Fig. 2. *A Ridge on the Soufrière at about 600 feet.*


Ash
New Vegetation,
Creepers, Ipomeas, very
common, called Ipomea
Learii in Northern
Islands
of
1902
Old Ash
Dry bed of Torrent


Creepers
on dead
Trees
Ridge
Ash washed away
from slopes · Vegetation
returning in
old soil
Creepers,
Ipomeas etc.
Consolidated
Ash


Ash
New Vegetation,
Creepers, Ipomeas, very
common, called Ipomea
Learii in Northern
Islands
of
1902
Old Ash
Dry bed of Torrent

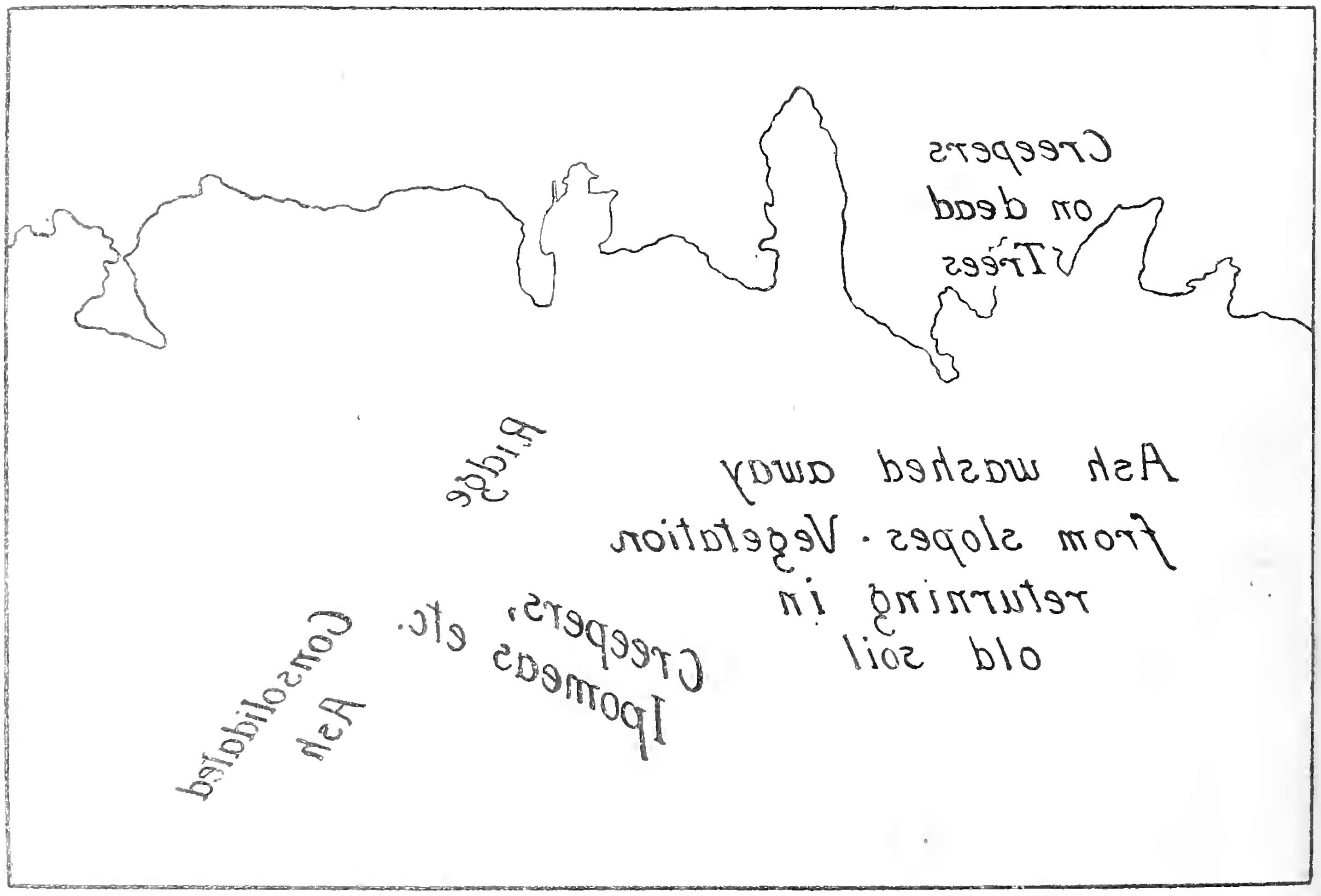

Creepers
on dead
Trees
Ridge
Ash washed away
from slopes · Vegetation
returning in
old soil
Creepers, etc.
Ipomeas
Consolidated
Ash

Fig. 1. *North Wall of Trespé Valley.*

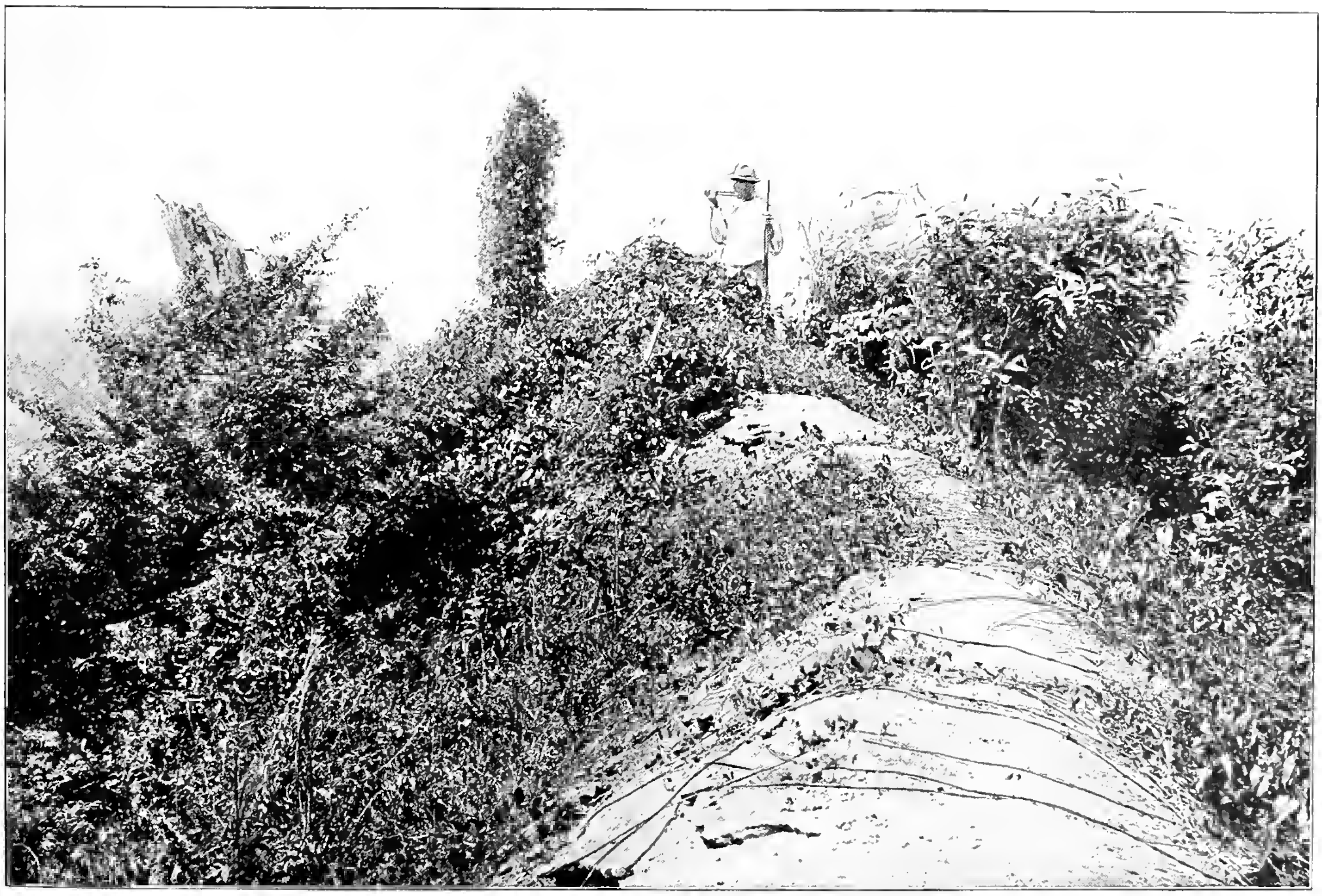


Fig. 2. *A Ridge on the Soufrière at about* 600 *feet.*

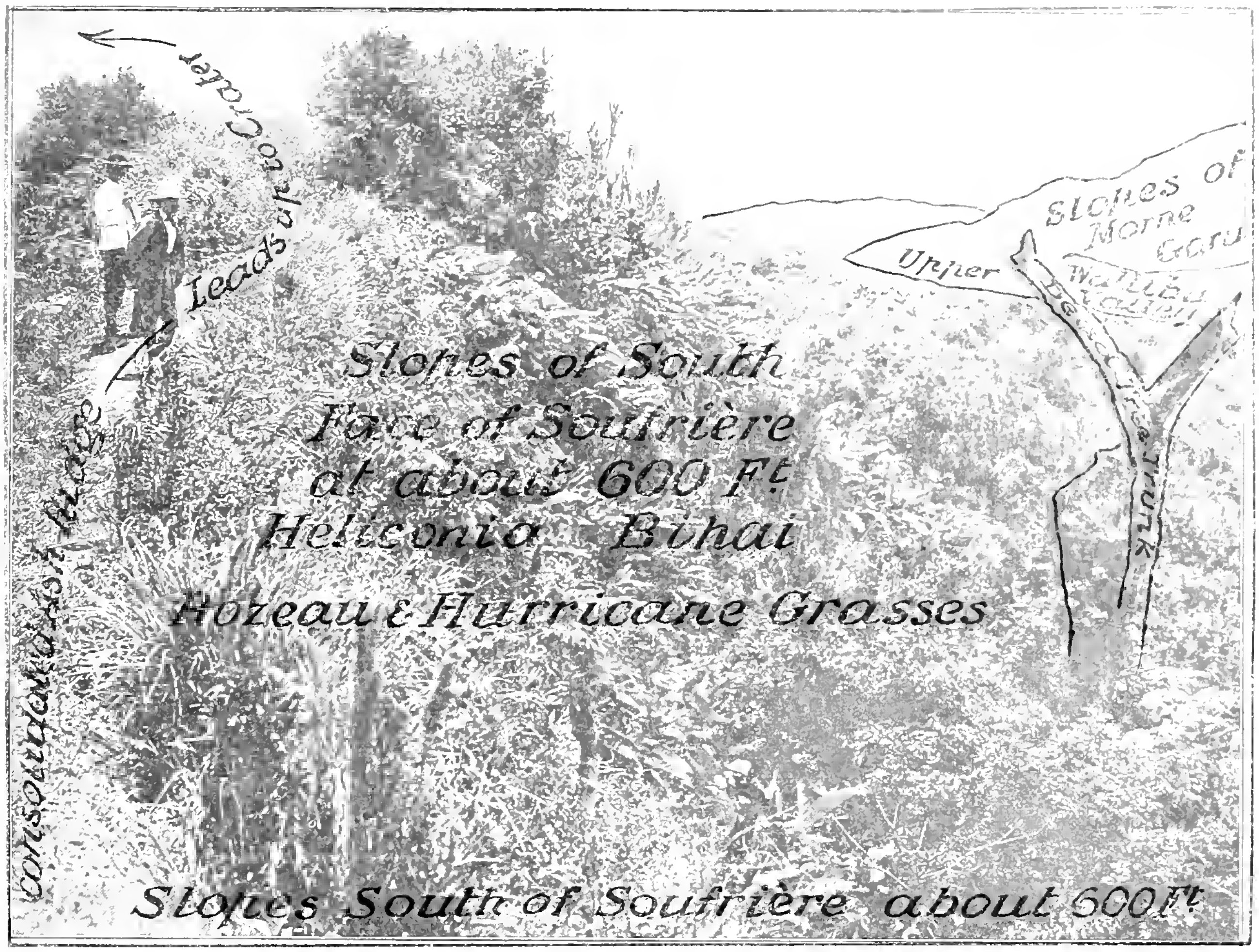


Fig. 1. *South Slopes of Soufrière at about 600 feet.*

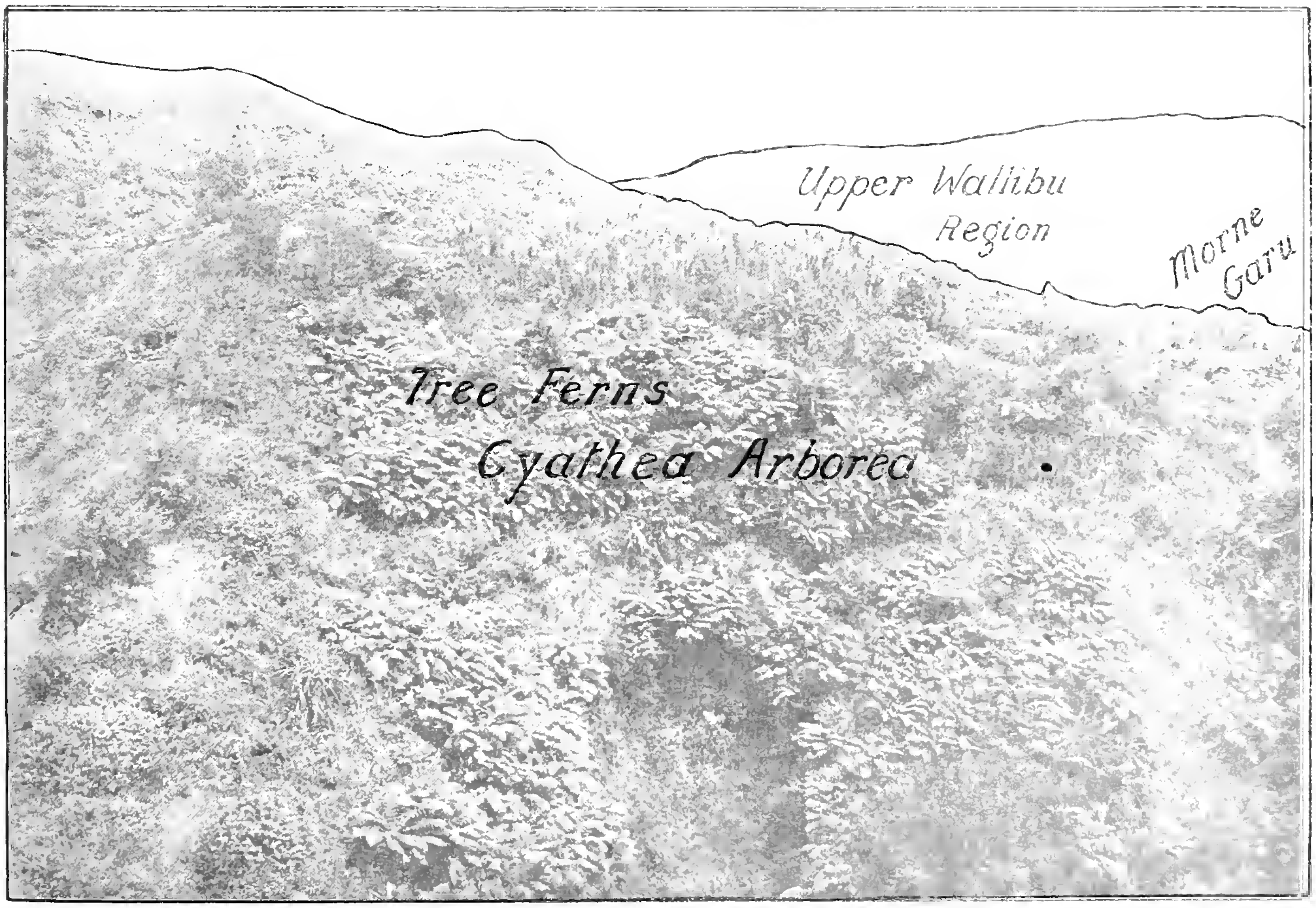
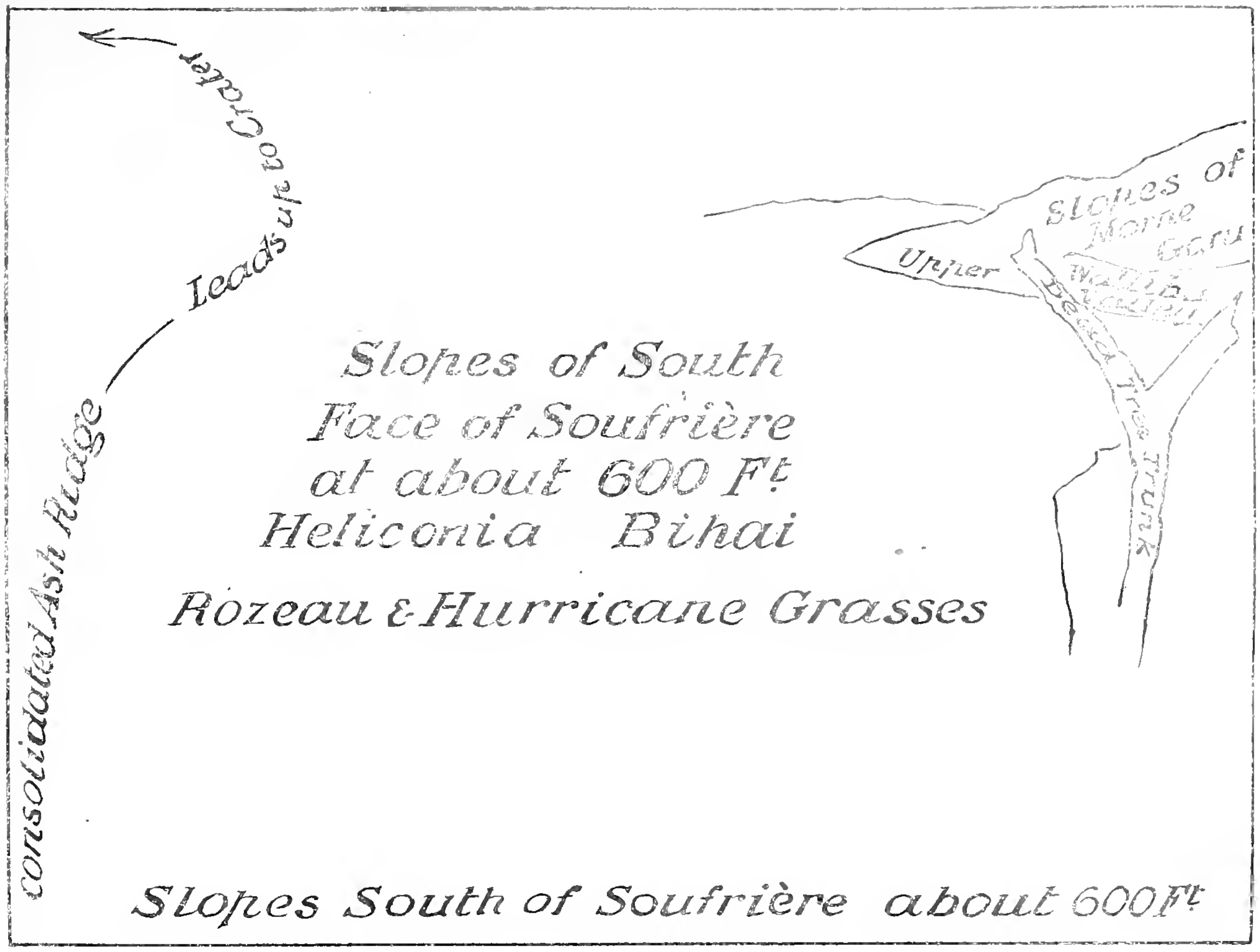
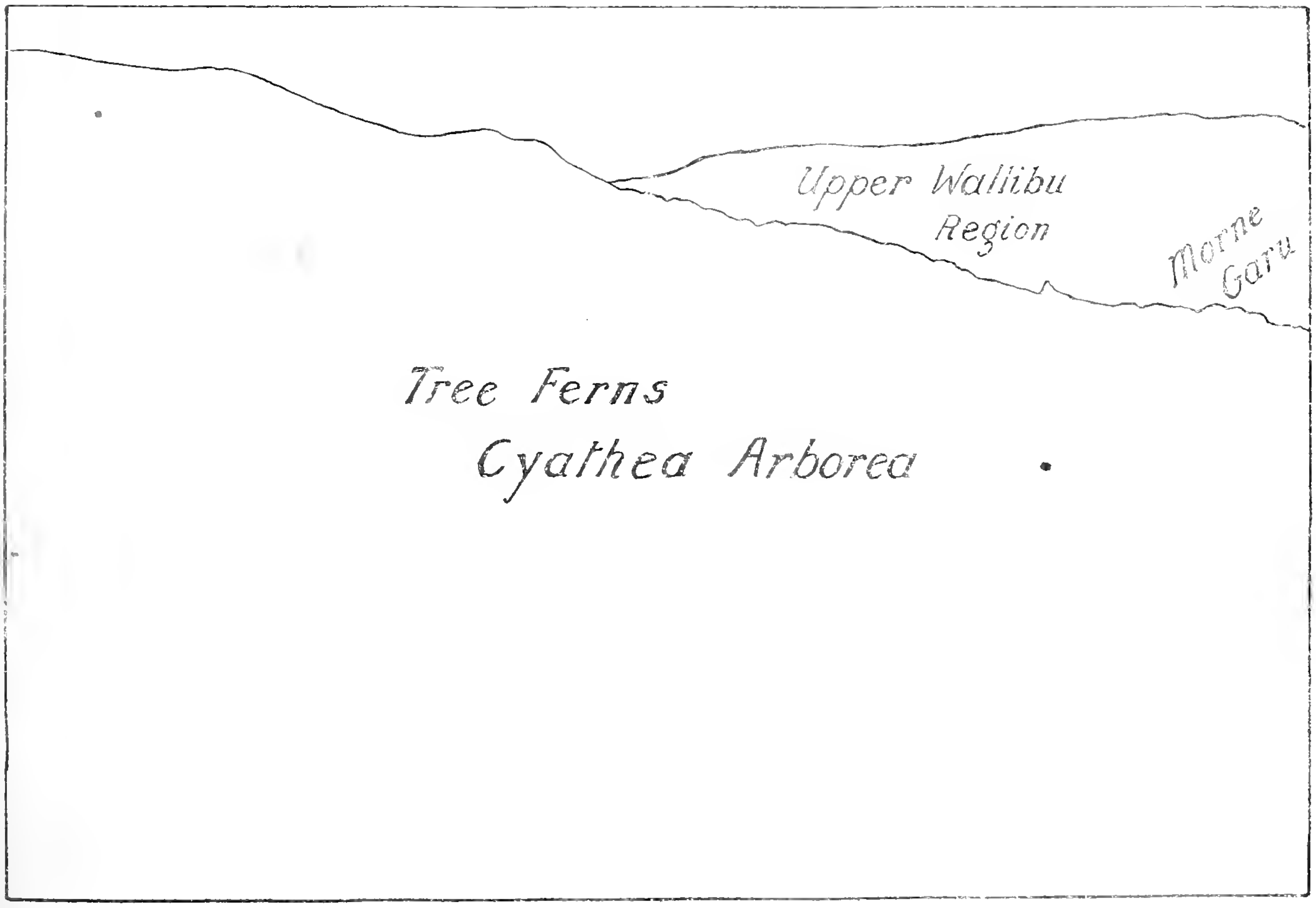
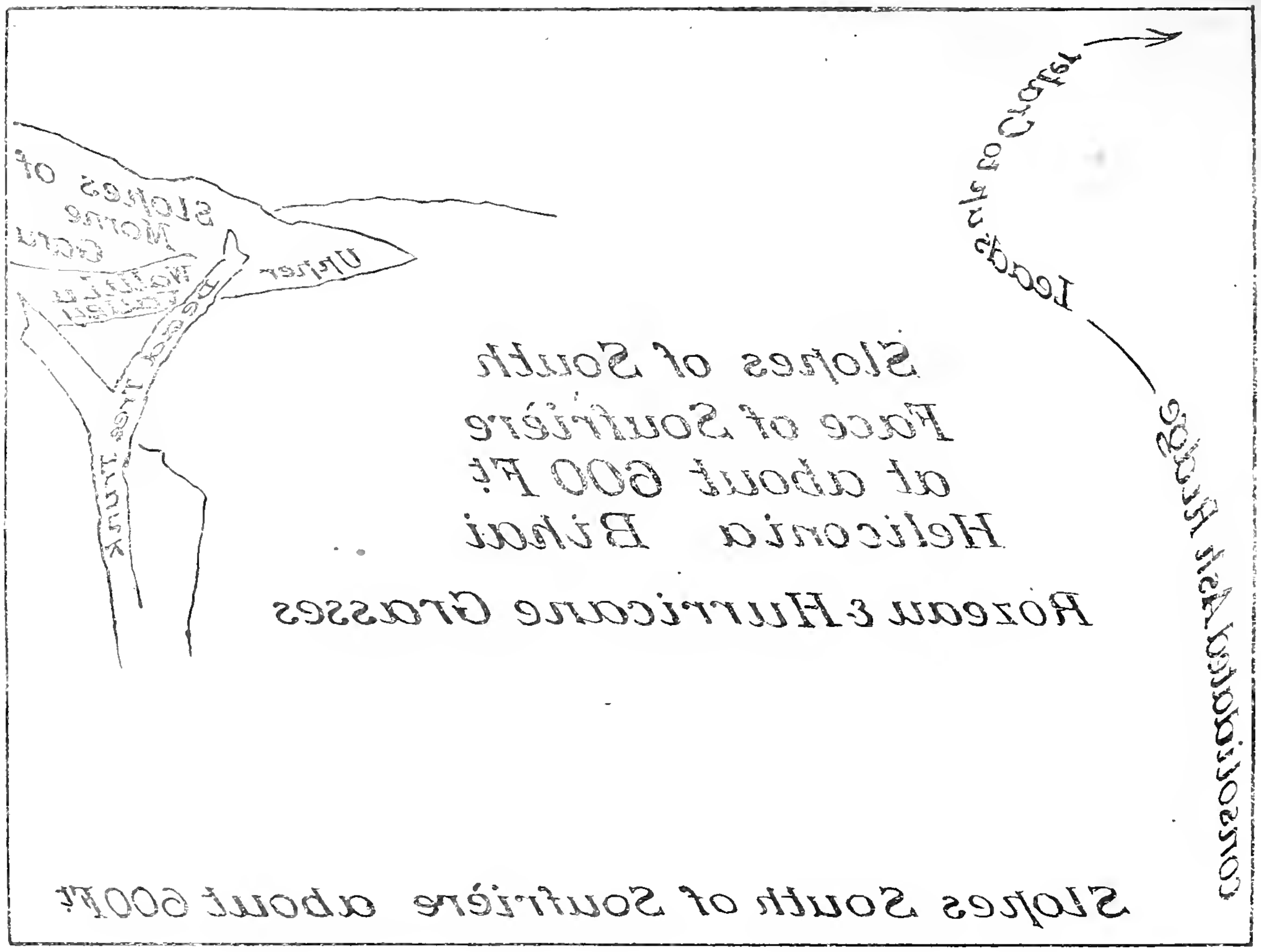


Fig. 2. *Slopes of Soufrière at about 800 feet.*



Slopes South of Soufrière about 600Ft




Slopes of Morne Garu
Upper Wallibu Region
Tree Fern Trunk
Leads up to Crater
Consolidated Ash Ridge
Slopes of South Face of Soufrière at about 600 Ft
Heliconia Bihai
Rozeau & Hurricane Grasses
Slopes South of Soufrière about 600 Ft

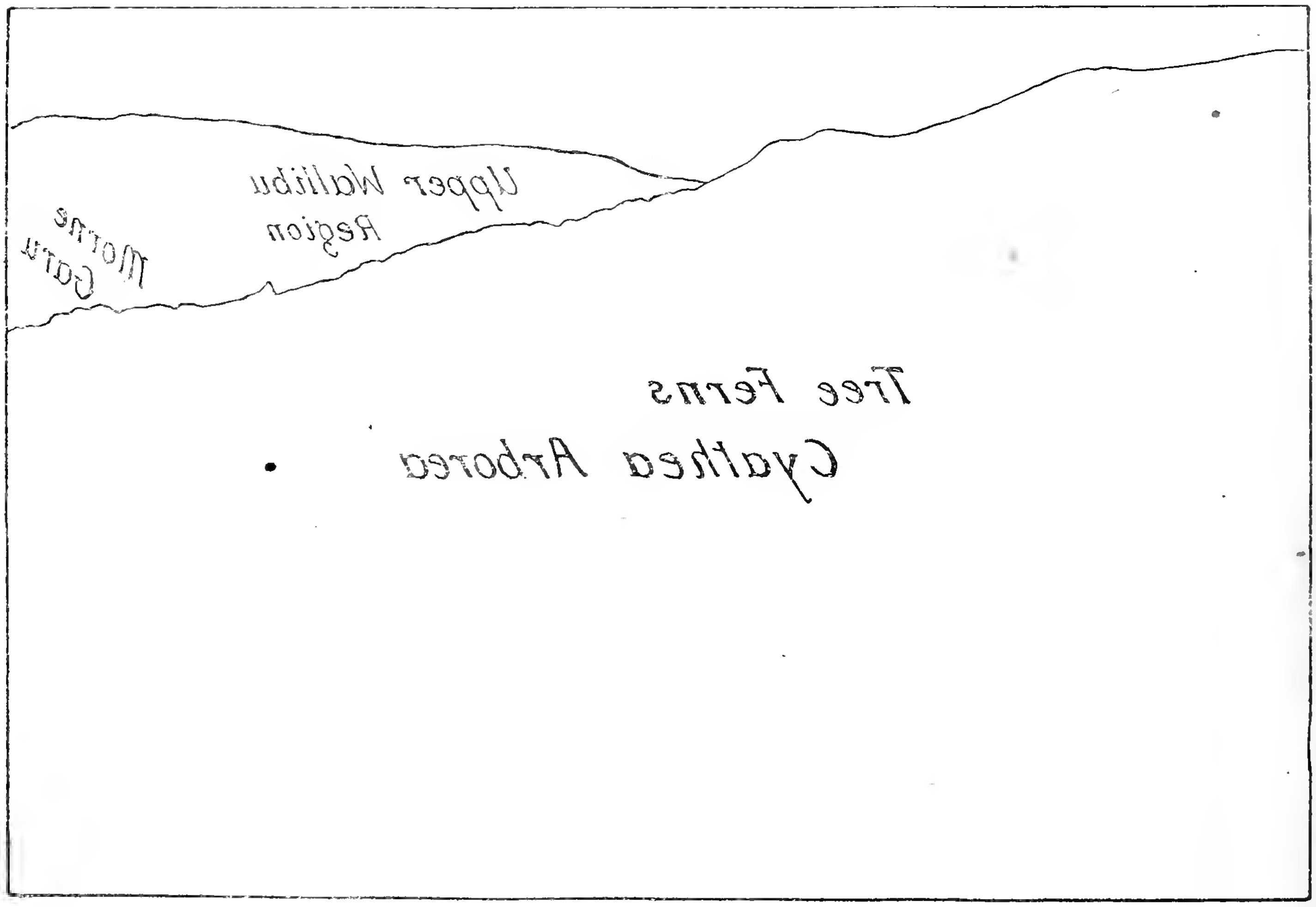

Morne Garu
Upper Wallibu Region
Tree Ferns
Cyathea Arborea

Fig. 1. *South Slopes of Soufrière at about* 600 *feet.*

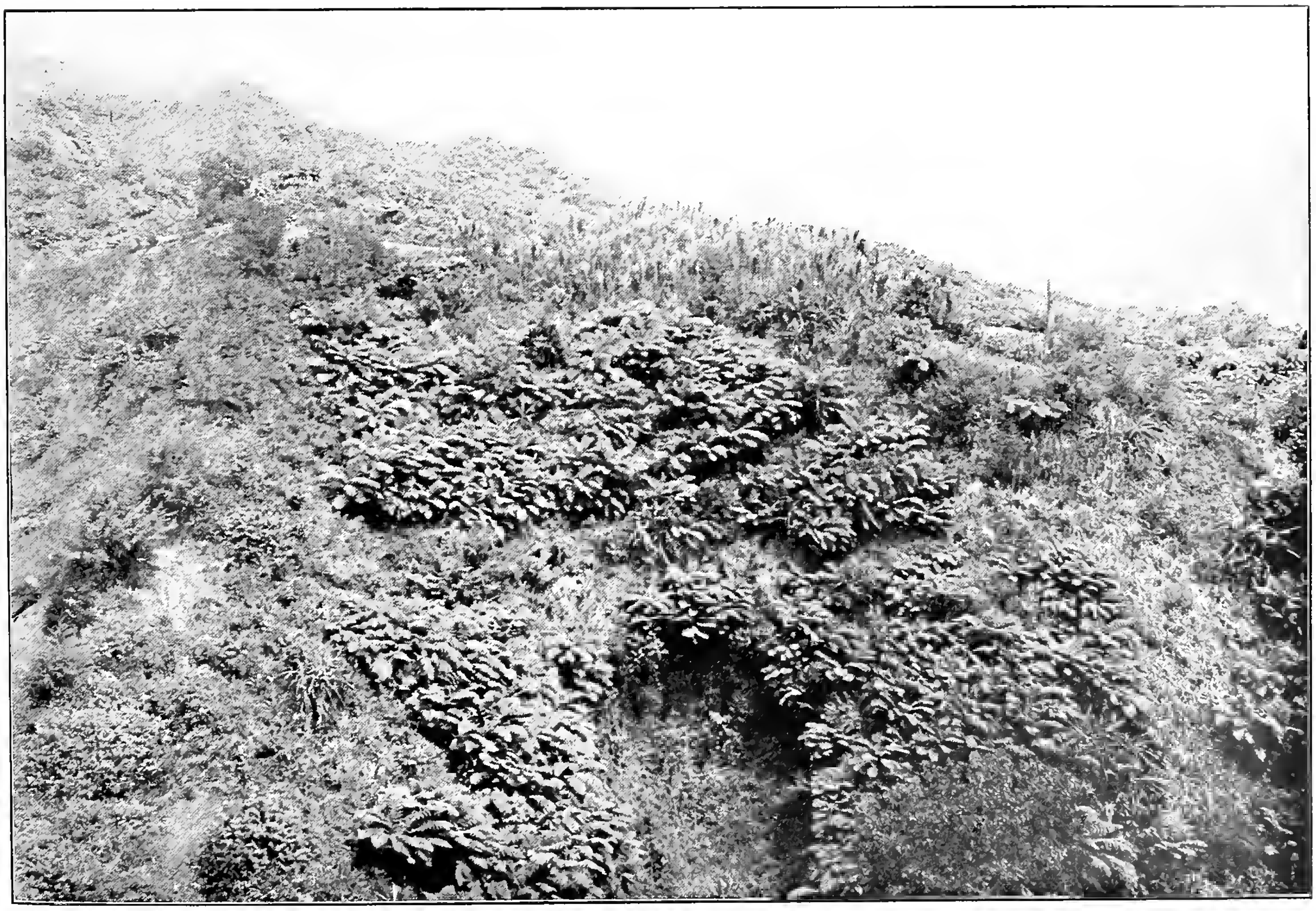


Fig. 2. *Slopes of Soufrière at about* 800 *feet.*

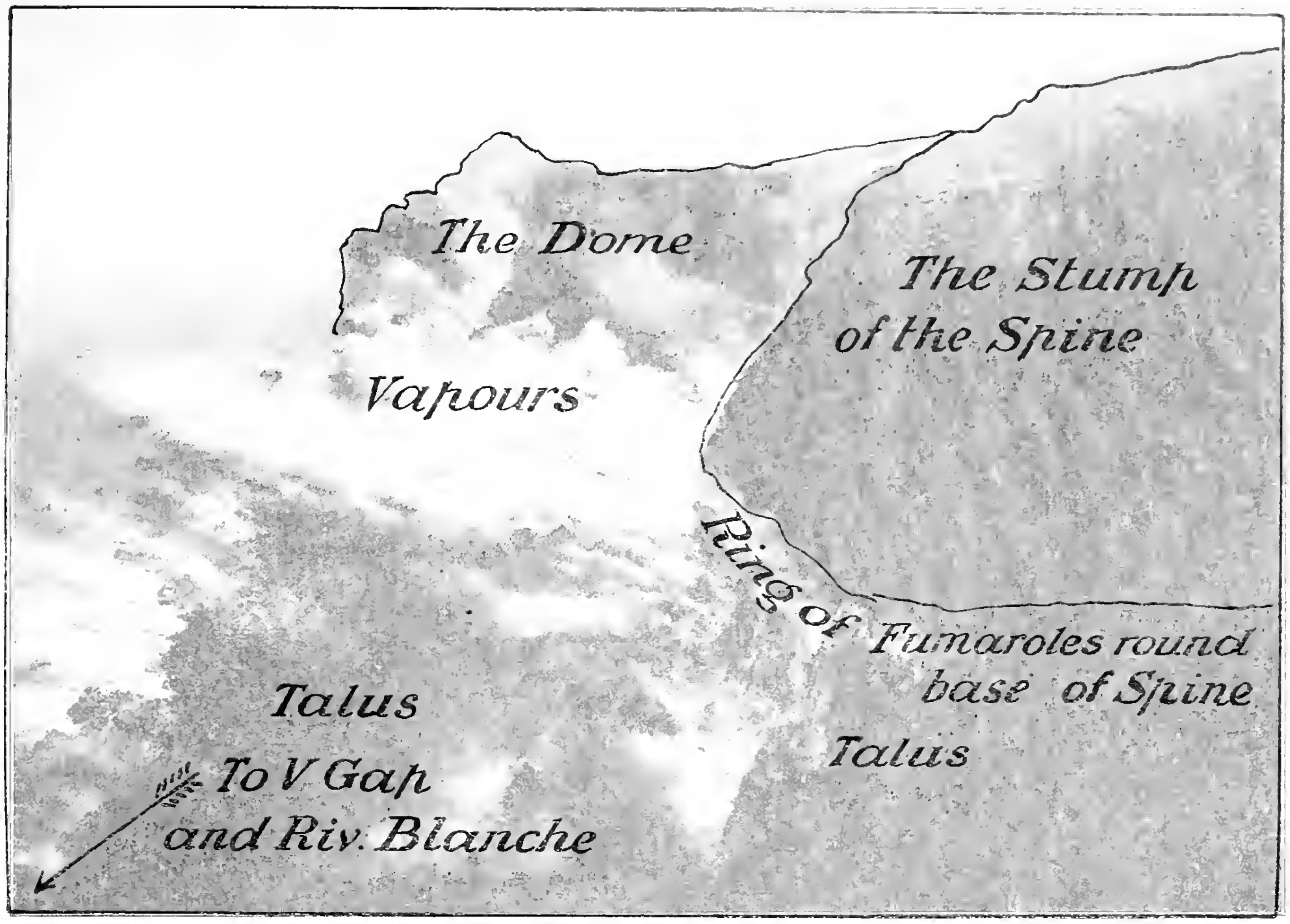


Fig. 1. *The Crater of Montagne Pelée, March 13, 1907.*

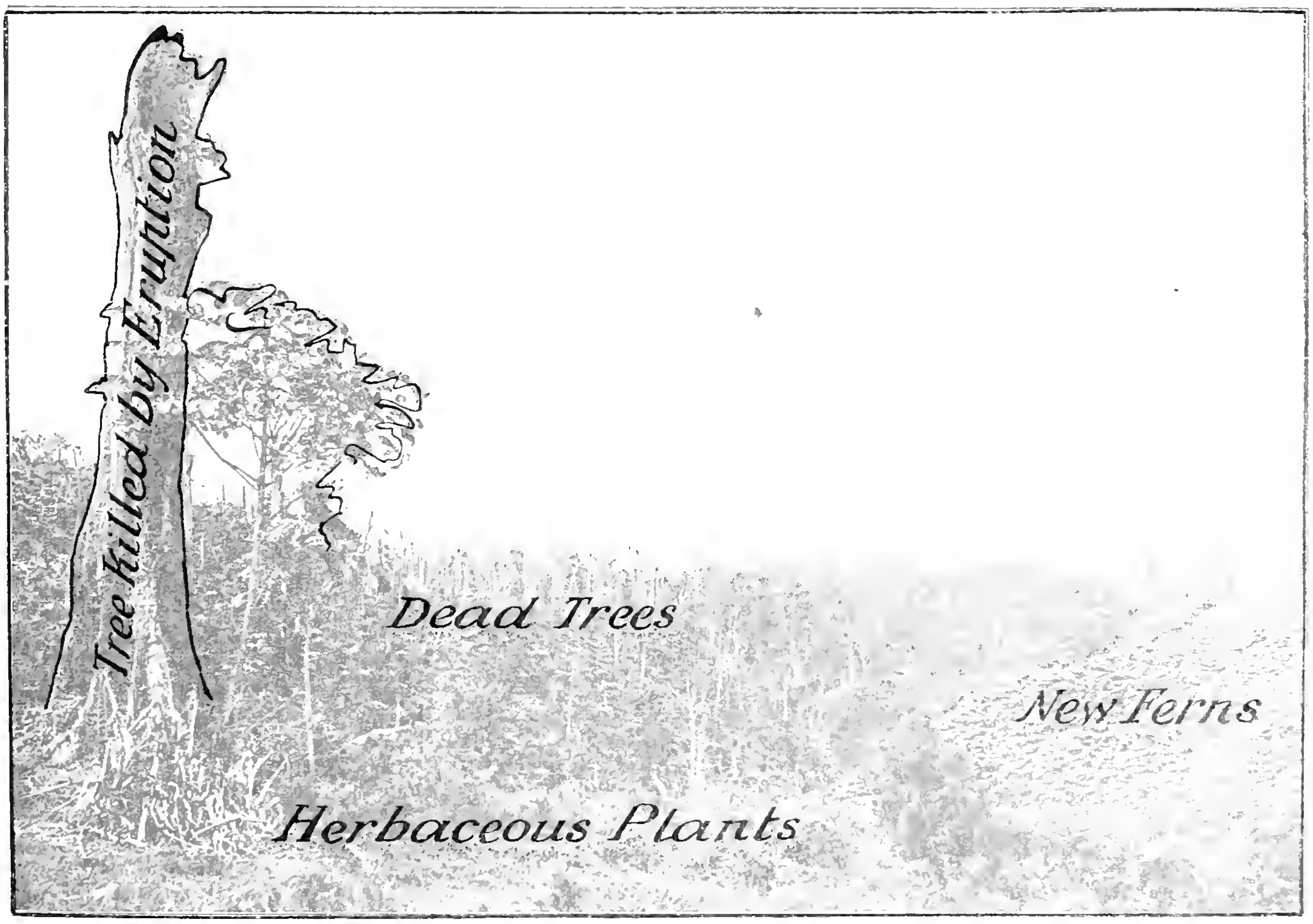
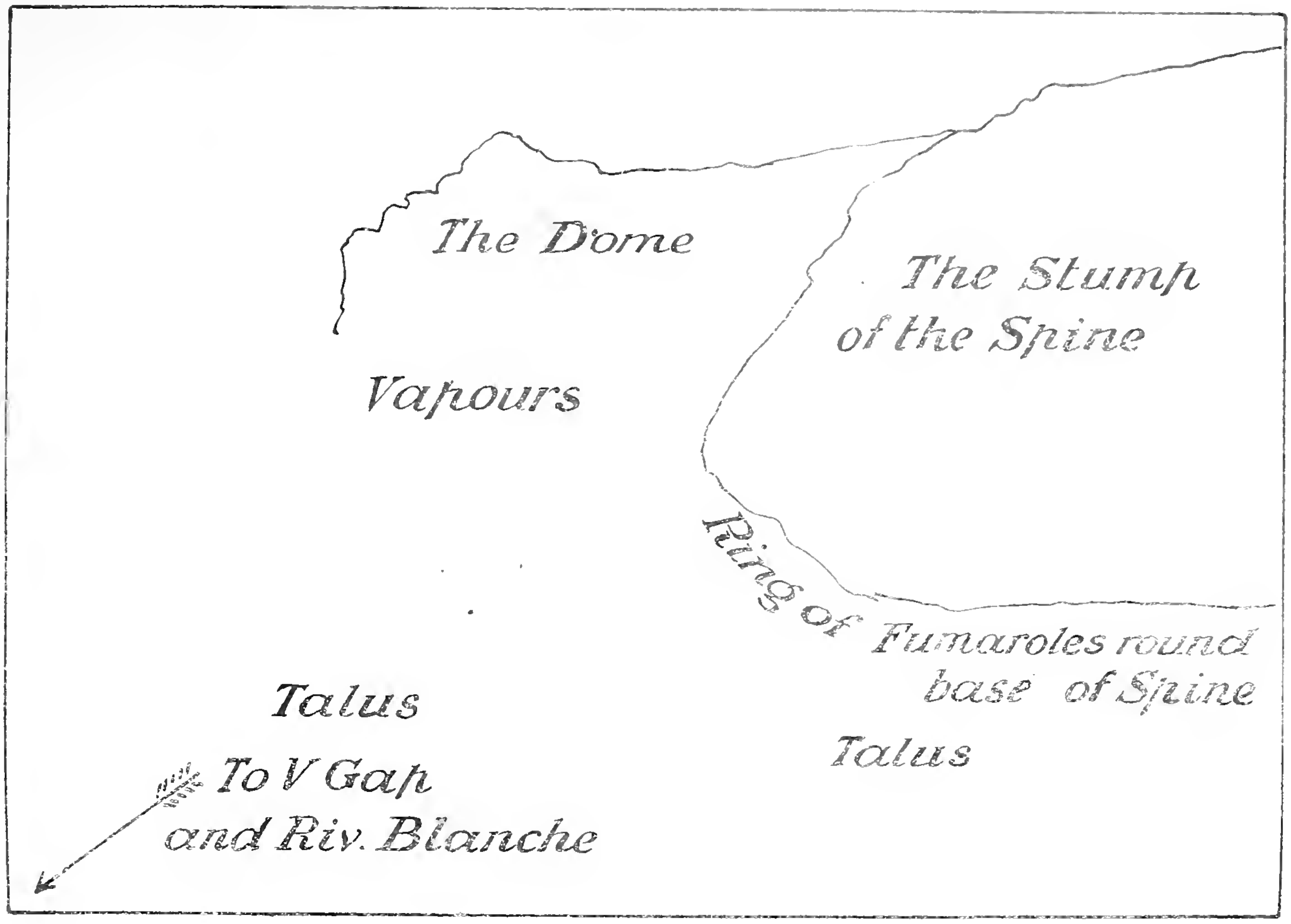
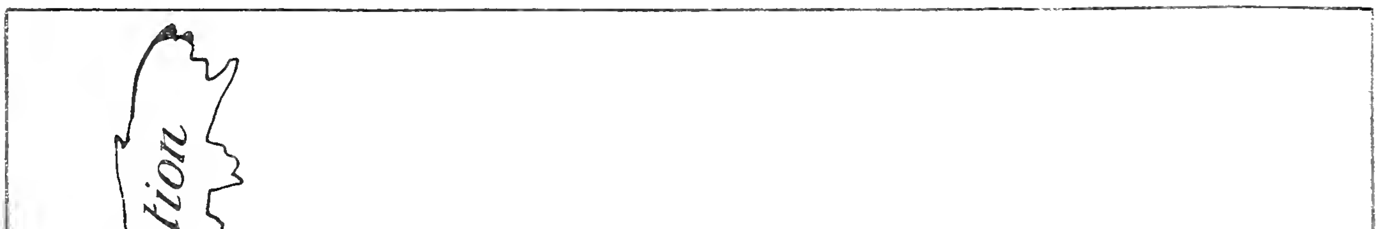


Fig. 2. *On Montagne Pelée, North side, at about 1500* [illegible]


The Dome
The Stump of the Spine
Vapours
Ring of Fumaroles round base of Spine
Talus
Talus
To V Gap and Riv. Blanche


Tree killed by Eruption
Dead Trees
New Ferns
Herbaceous Plants

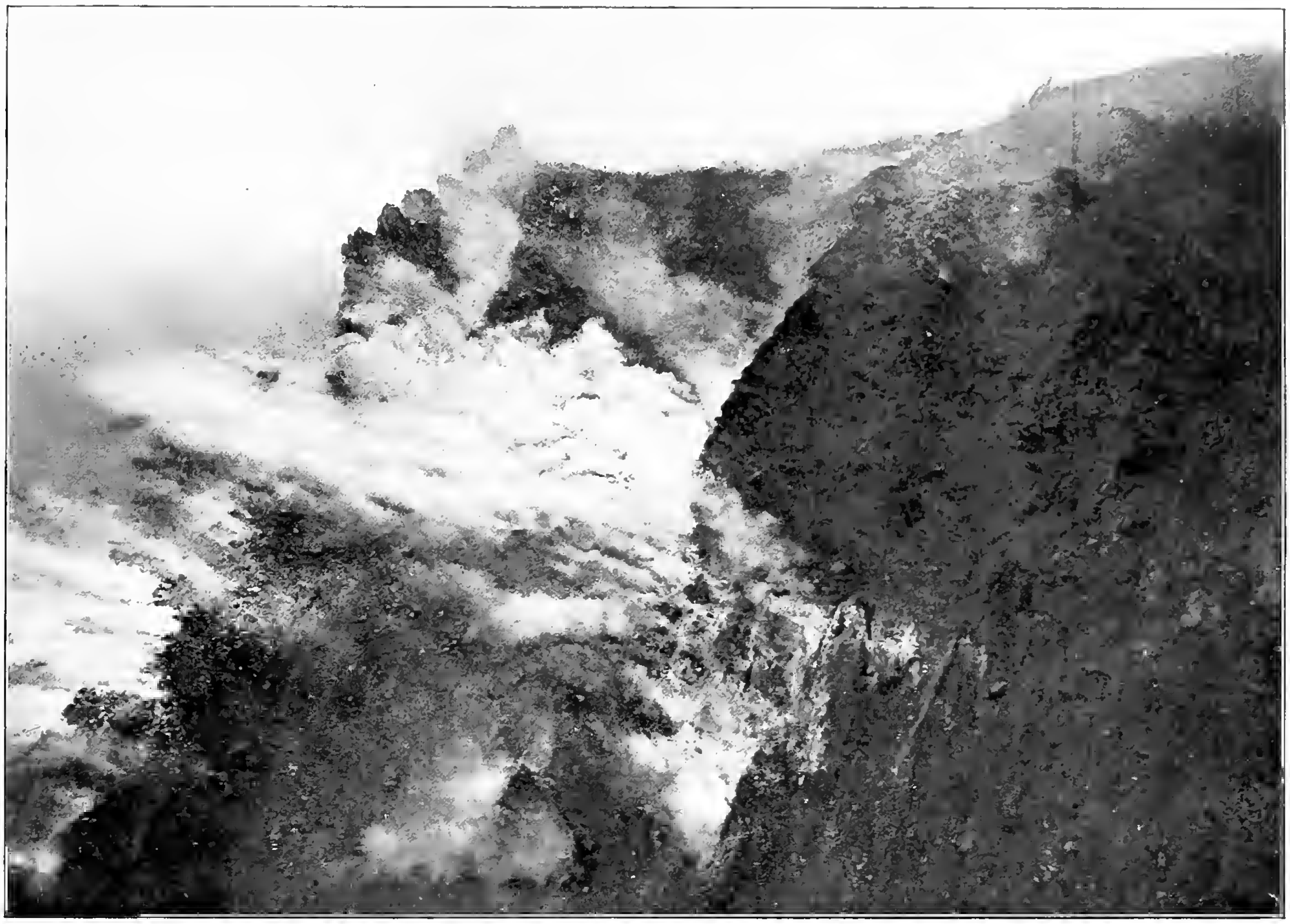


Fig. 1. *The Crater of Montagne Pelée, March* 13, 1907.

Fig. 2. *On Montagne Pelée, North side, at about* 1500 *feet.*

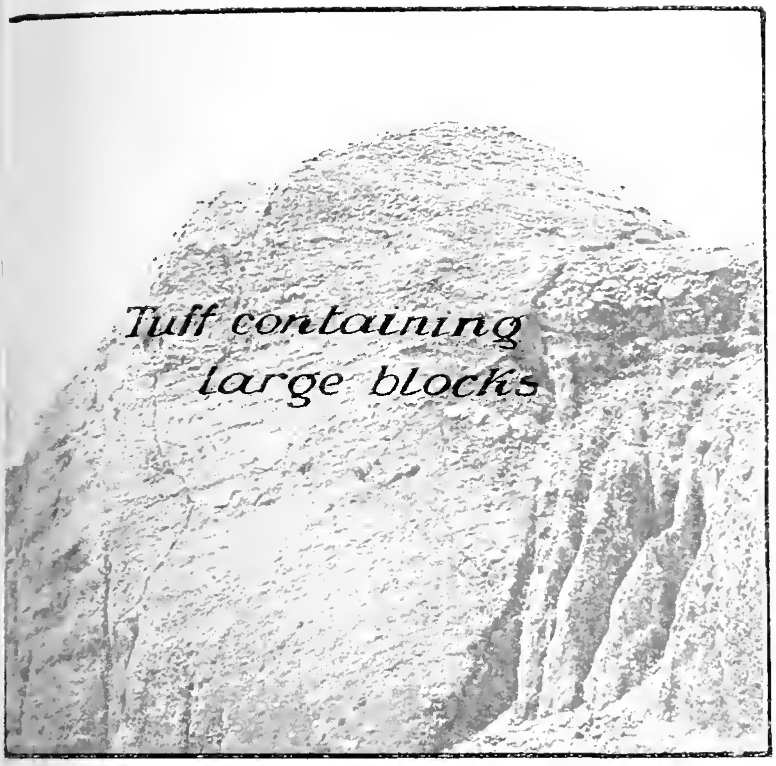


Fig. 1. *Tuff-agglomerate, scored by avalanches. General view.*

Fig. 2. *Details beyond left corner of Fig. 1.*

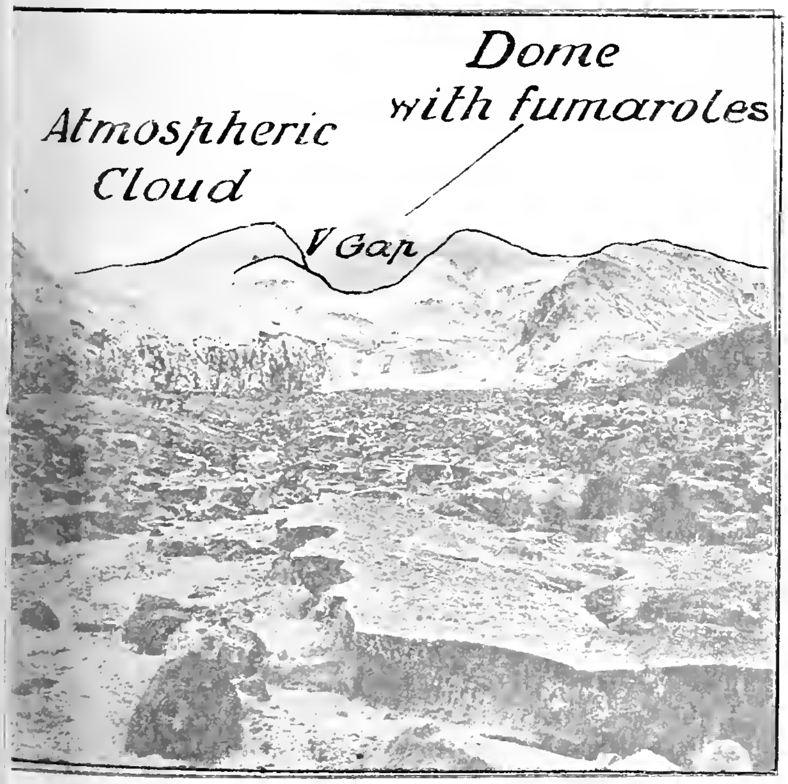


Fig. 3. *Valley of Rivière Blanche, from near shore.*

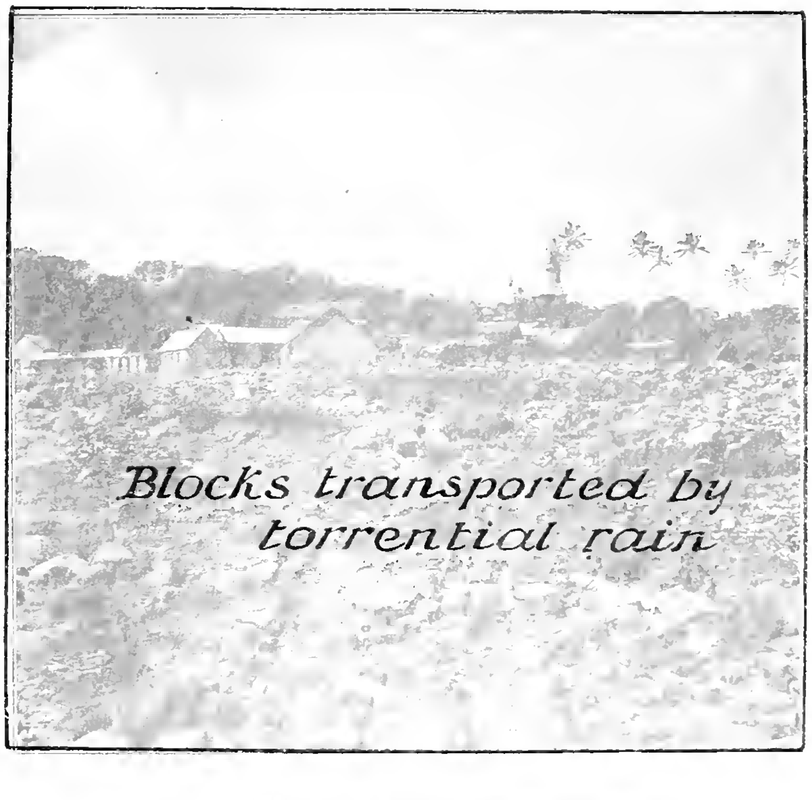
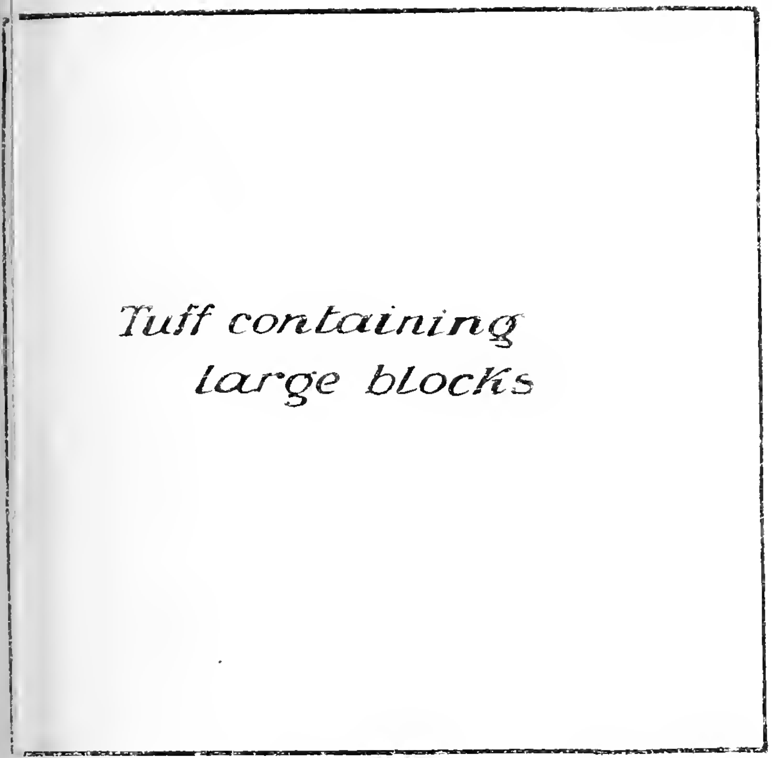
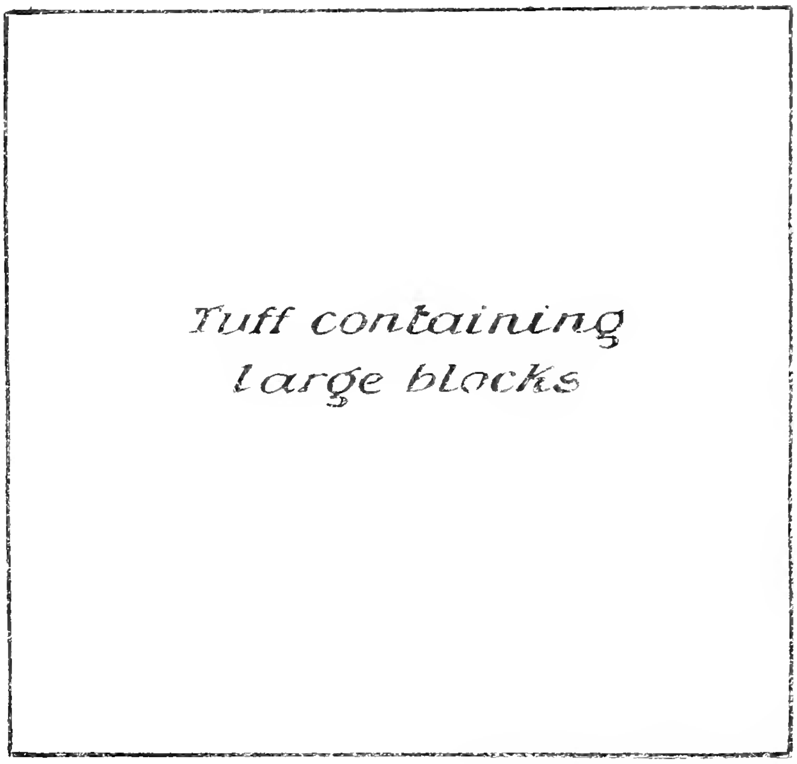
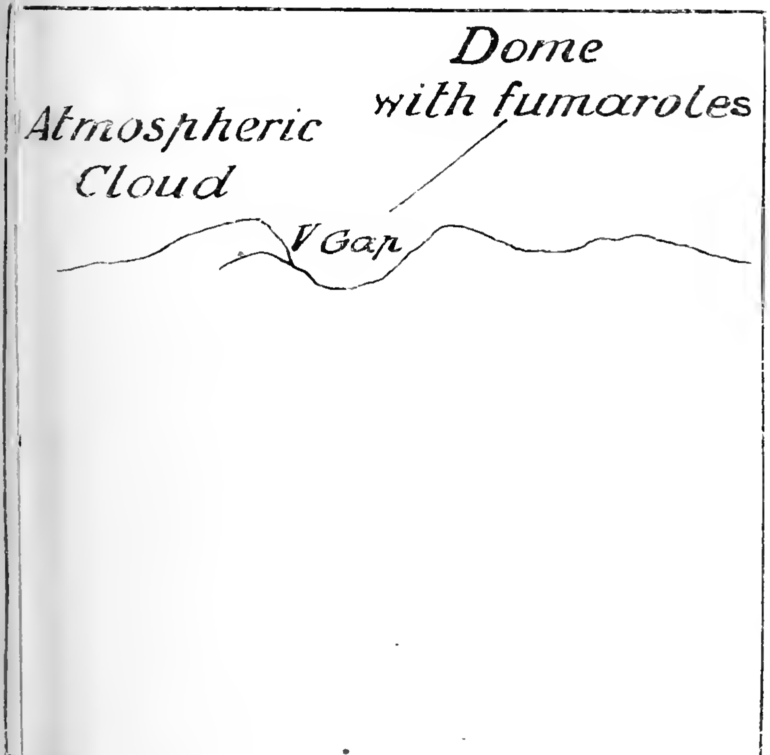
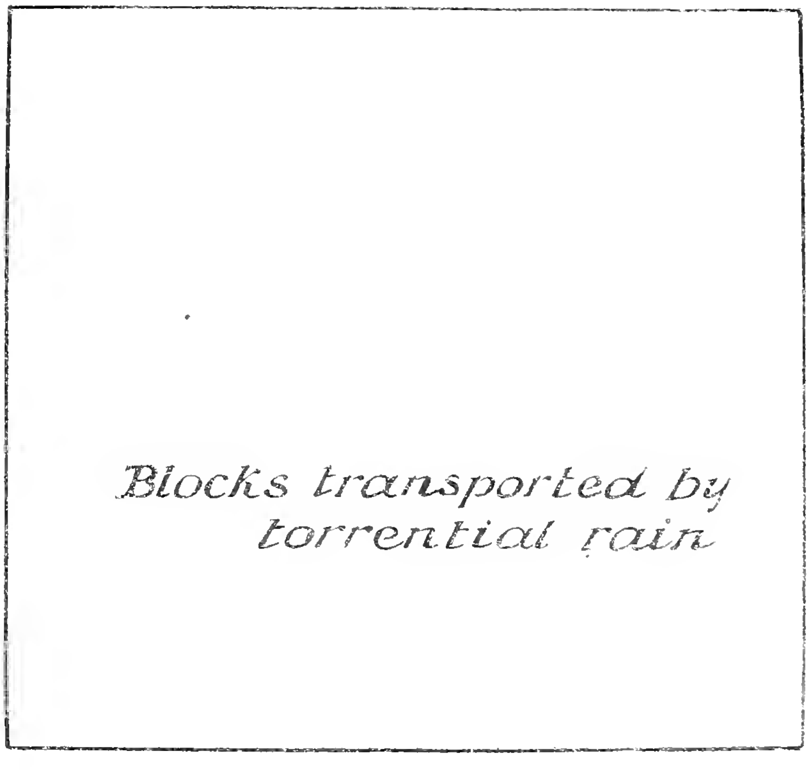


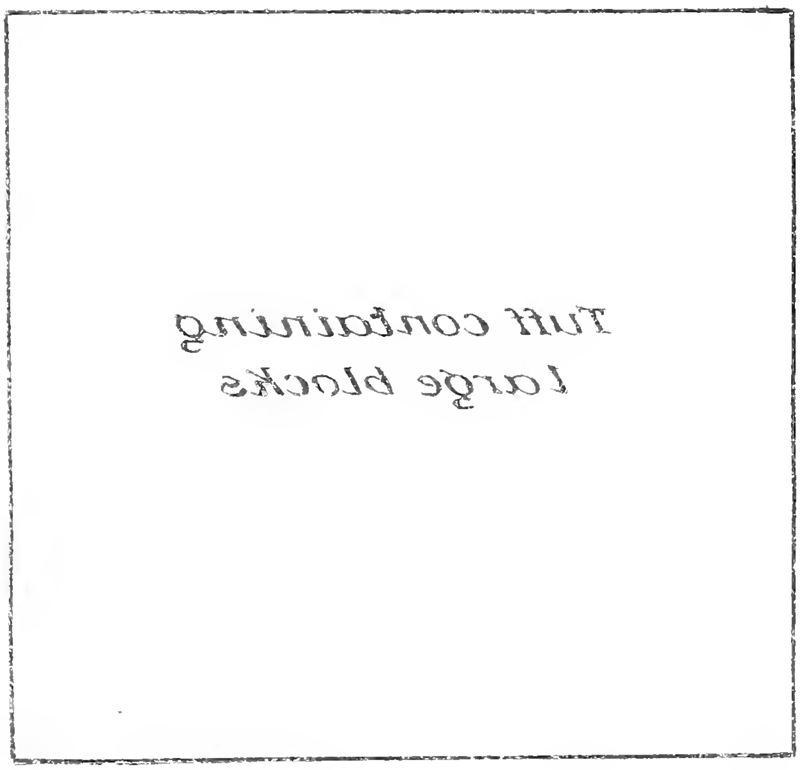
Fig. 4. [illegible]

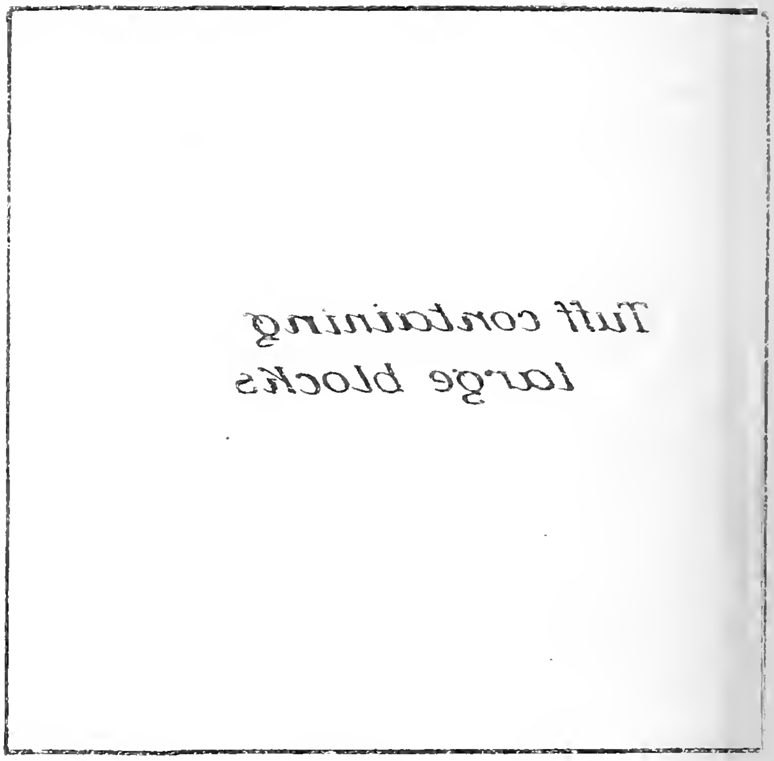

Tuff containing large blocks

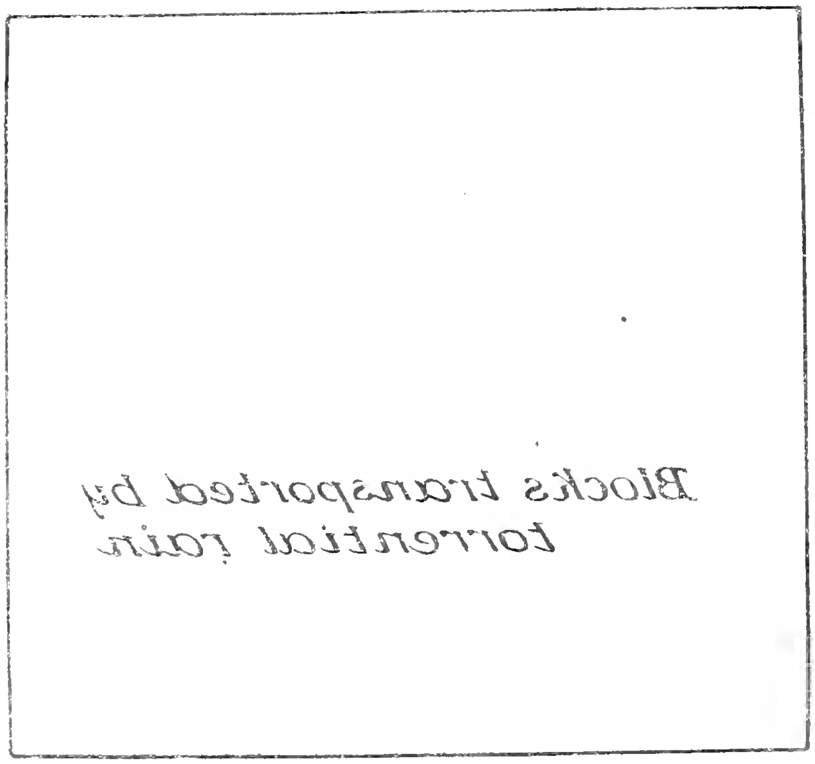

Tuff containing large blocks

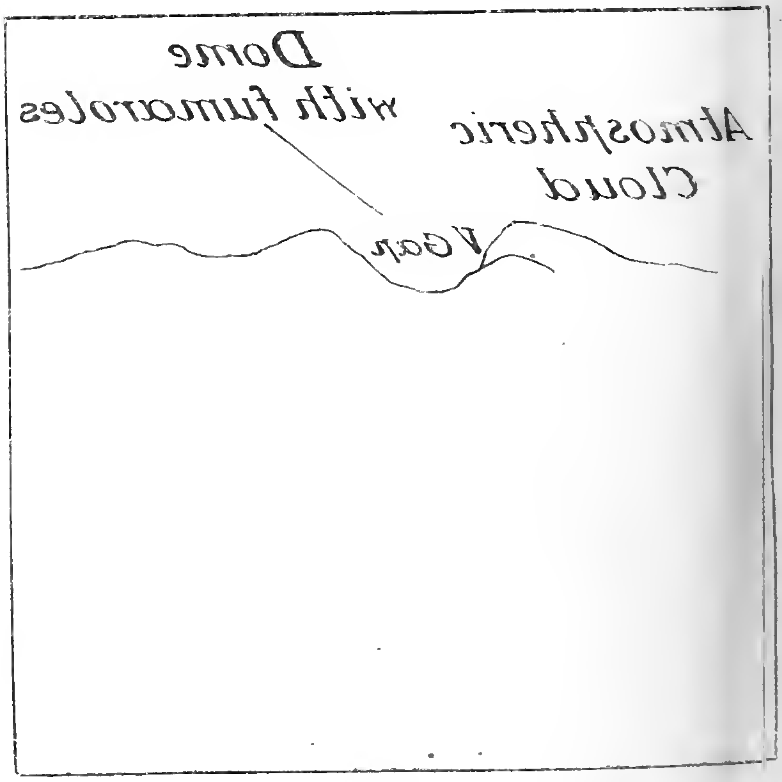

Dome with fumaroles
Atmospheric Cloud
V Gap

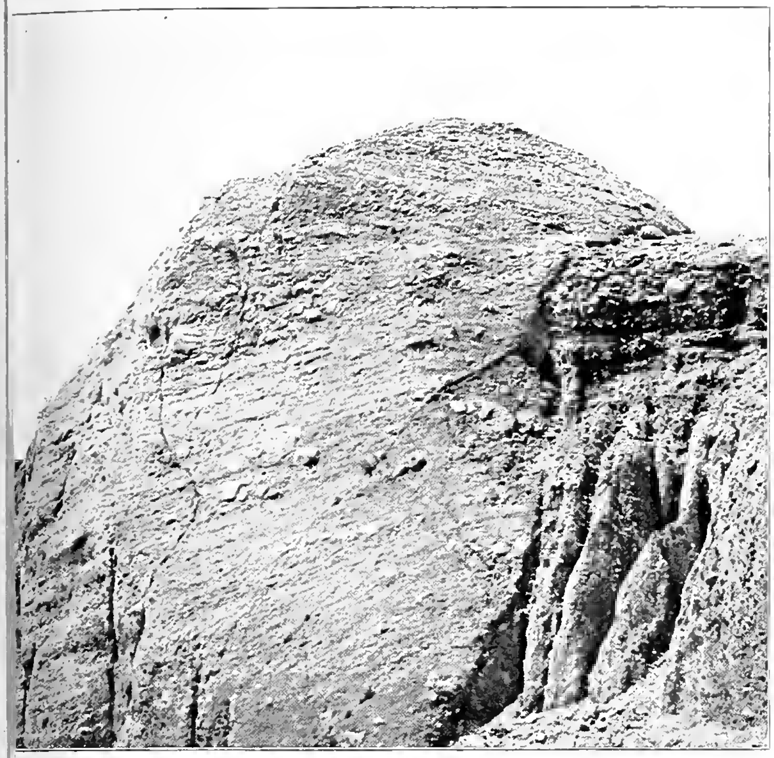

Blocks transported by torrential rain


Tuff containing
large blocks


Tuff containing
large blocks


Blocks transported by
torrential rain


Dome
with fumaroles
Atmospheric
Cloud
V Gap



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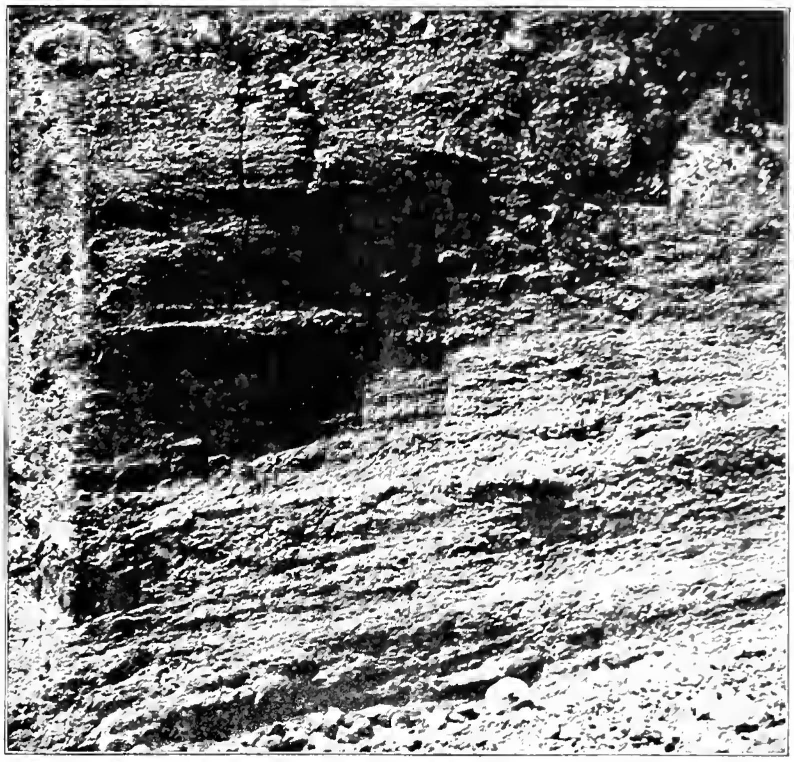

Fig. 2. *Details beyond left corner of Fig.* 1.

Fig. 3. *Valley of Rivière Blanche, from near shore.*

Fig. 4. *The new Delta at Basse Pointe.*

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[Plates 26–27.]

PETROGRAPHICAL NOTES ON THE PRODUCTS OF THE ERUPTIONS OF MAY, 1902, AT THE SOUFRIÈRE IN ST. VINCENT

BY

JOHN S. FLETT, M.A., D.Sc.

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VIII. *Petrographical Notes on the Products of the Eruptions of May,* 1902, *at the Soufrière in St. Vincent.*

By John S. Flett, *M.A., D.Sc.*

Communicated by H. B. Woodward, *F.R.S.*

Received January 20,—Read January 23, 1908.

[Plates 26-27.]

Contents.

The rocks collected during our visit to the West Indies, in 1902, included specimens of the ashes, ejected blocks, &c., cast out by the eruptions of May, and of such lavas, belonging to previous eruptions of the Soufrière and the extinct volcanoes of the south part of the island, as were in good preservation and easily accessible from our line of route. We are also indebted to Mr. Macdonald, Mr. Darrell, and other inhabitants of St. Vincent, and to Sir Daniel Morris and the officers of the Imperial Agricultural Department for the West Indies acting under him (more particularly to Mr. Henry Powell, Curator of the Botanic Station, St. Vincent), for specimens sent us after our departure for England. Professor Lacroix has very kindly furnished us with specimens of the older rocks of St. Vincent, which he collected during his visit, and of an ejected block containing cordierite, which he found on the edge of the crater in January, 1903.

The Ejecta of the Eruptions of May, 1902.

Among the materials ejected during May, 1902, there were not only ashes and sand, with volcanic bombs which were derived from the active magma within the crater, but also large quantities of the older rocks of the mountain which had been torn from the walls of the crater and were mingled with the new ashes. The difficulties of collecting from the deposits of hot sand laid down by the avalanche were considerable, as the principal stream sections of the new materials were too hot and too unstable to be approached. Fragments lying on the surface of the avalanche evidently belonged to the most recent stages of the volcanic activity. The deeper parts of the new deposit were usually inaccessible, but where the secondary steam explosions had built small cones on the rivulets it was easy to collect blocks that had been projected from the interior of the beds of hot ash. These form the major part of the ejected blocks of 1902 contained in our collections.

The ashes and sand gathered in Barbados, Kingstown, Chateaubelair, and other localities during May, 1902, and at subsequent times can, of course, be assigned at once to their respective eruptions, and, with the large semi-vitreous bombs scattered over the surface of cultivated grounds on both the windward and leeward sides of the island, may be taken as satisfactory evidence of the nature of the new magma within the crater. It seems clear, however, that some of the previous eruptions produced bombs not essentially differing from those of 1902, and these can only be distinguished by the traces of decomposition they sometimes show, or by the positions in which they are found.

Volcanic Sand and Dust.

As stated in the first part of this report, fine sand and dust formed the greater part of the hot avalanche, and were the only materials transported to a considerable distance. The Barbados dust has been described by several writers,* and is now well known to most of those who are interested in volcanoes. We have also examined specimens from Kingstown, Calliaqua, and other localities in the south part of St. Vincent, and from Wallibu, Georgetown, and the southern flanks of the Soufrière. These have a great similarity in general character, though they may not be of

---

* Flett, John S., "Note on a Preliminary Examination of the Dust that fell in Barbados after the Eruption in St. Vincent" 'Quart. Jour. Geol. Soc.,' vol. 58, p. 368 (1902). Falconer, John D., "Volcanic Dust from the West Indies," 'Nature,' vol. 66, p. 132 (1902). Porter, T. C., "Volcanic Dust from the West Indies," 'Nature,' vol. 66, p. 131 (1902). Klein, C., "Ueber die am 7. Mai 1902 vom Vulkan Soufrière auf St. Vincent ausgeworfene vulkanische Asche," 'Sitzb. Berlin. Akad.,' 1902, p. 992. Diller, J. S., "Volcanic Rocks of Martinique and St. Vincent," 'National Geographic Magazine,' vol. XIII., p. 285 (1902). Smith, Longfield, "Volcanic Eruptions in the West Indies," 'West Indian Bulletin,' vol. III., p. 271 (1902).

absolutely identical origin. Those that were carried to some distance were emitted from the crater during the height of the paroxysm of the afternoon of May 7th. Those gathered near the Soufrière may have been mixed with materials emitted at a subsequent time, either during the first or second eruption (May 7th and 18th, 1902). Sand from the Soufrière contains, as might be expected, a larger number of fine lapilli; the Barbados dust consists mainly of single crystals, or fragments of crystals, with small grains of more or less vitreous character. But the same ingredients occur in all the dusts in very much the same proportions. There are slight differences in the relative abundance of the component minerals which can be traced very clearly in the chemical analyses of samples from different localities (see p. 311), but these differences are not great.

Sir Daniel Morris has sent us samples of the Barbados dust-fall of May 7th and 8th, 1902, collected at different hours. These show that the material which fell during the later hours was finer grained and rather more pale coloured than that which fell earlier. It is to be expected that as the dust cloud was at a great height the coarser and heavier minerals would first subside. Fragments of broken felspar crystals and of glass are distinctly more common in the later part of the dust-fall and account for its paler colour.

The most striking feature of these dusts is the large proportion of crystalline minerals they contain, and this led us to bring forward the hypothesis that the magma, "or at least the upper part of it which gave rise to the great black cloud, was to a large extent crystallised, contained comparatively little fluid matter, and was accordingly near the temperature of consolidation, or may even in part have solidified already" (Report, Part I., p. 523). This hypothesis received the most unexpected confirmation at a slightly later period when it was announced that the magma in Pelée was being extruded as a solid vertical column or obelisk which attained at one time a height of 900 feet.

Of the minerals of these dusts the most abundant is plagioclase felspar. Its crystals are often broken, but the smaller may be perfect, especially when they have an adherent pellicle of glass. Optical and specific gravity tests, especially the extinctions of cleavage flakes, show that they range from labradorite to basic bytownite (An 50 per cent. to An 84 per cent.). They are full of glass enclosures, often of regular shape, with fixed bubbles. Zonal structure is very common in them; in fact, they present similar characters to those of the phenocrysts in the bombs, to be described later. The commonest faces are 001, 010, 110, $1\bar{1}0$, $10\bar{1}$, $20\bar{1}$. The augite is pale brownish-green, very slightly pleochroic in thick grains. Good crystals are rare and show 100, 010, 110, 111. The extinction angle $Z : c$ is about 45 degrees. Hypersthene is always present in considerable amount and often its crystals are very perfect. Their faces are 100, 010, 110, and probably 111. Frequently the crystals are broken across, along planes of fracture perpendicular to the prism axis; they then show squarish octagonal outlines with the pinacoids larger than the prism faces.

The pleochroism is strong and is of the usual character. The optic axial angle (negative) is large (2E over 120 degrees, 2V over 60 degrees). Glass enclosures and grains of magnetite are common in the pyroxenes. Olivine occurs in small grains; perfect crystals are not found, but only splinters which often show a conchoidal fracture. It is colourless or pale brown (perhaps from oxidation in presence of hydrochloric acid gas and air), and its presence is easily confirmed by treating the powder with strong cold acid when it is covered with a film of gelatinous silica, even before the basic felspars are attacked. Hornblende, as reported by FALCONER and KLEIN,* is found occasionally. So far as we have seen it is always brownish-green and occurs only in irregular fragments. Most of the iron oxide is titaniferous magnetite in small rounded grains; pyrites, apatite, and possibly zircon are also present.

Non-crystalline or glassy material occurs in all the dusts, though less abundant than the crystals. It is partly in minute fragments, partly in thin films surrounding the crystals, and partly in the form of small, rounded vesicular lapilli. The steam cavities which abound in it are empty. Between crossed nicols some of these lapilli contain small crystals evidently belonging to the second generation, showing that crystallisation was preceding in this portion of the rock as it ascended in the crater. Much of the glass, however, is perfectly vitreous, and this portion was probably liquid at the moment of projection. Occasionally the glass has been drawn out into threads while still in a viscous state. The lapilli, however, are not highly pumiceous and the splinters do not have those arc-shaped, concave outlines which are found in shattered pumiceous glasses (*e.g.*, those emitted by Krakatoa in 1883).†

In the first part of this report we have stated our belief that the magma of the Soufrière, though in large part crystallised, was not entirely solid at the moment when it was shattered into dust and the great black cloud emerged from the crater. Professor LACROIX ‡ has found that the later *nuées ardentes* or Peléean clouds of Montagne Pelée were produced by the disruption of a solidified magma. But the facts of the eruption of May 7th in St. Vincent, as given by us in the first part of this report, are sufficient to prove that the magma was a semiliquid mass as it ascended in the crater. The crater lake was at its usual level at 11 a.m. on Tuesday (May 7th); at midday on Wednesday the lake was discharged by overflowing the southern lip of the crater. Thus in 24 hours it had risen about 1000 feet, or 40 feet per hour. Yet, according to the evidence of all who knew it before and have seen it since, the interior of the crater was not greatly modified and many of its old features were recognisable after the eruption. Only a plastic, semiliquid mass could have risen so rapidly and could have been ejected with so little disturbance and so little permanent alteration of the topography of the interior of the crater. The great rock column

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* *Loc. cit.*

† SYMONS, G. J., 'The Eruption of Krakatoa and subsequent Phenomena,' Plate 4 (1888).

‡ 'Montagne Pelée,' pp. 206, 208, 383.

which rose from the crater of Pelée in the latter part of 1902 proves that the magma, once solid, is not highly explosive.

The Bombs.

The slaggy black bombs, which were abundant especially on the surface of the new ash deposits in the valleys of the Wallibu and the Rabaka Dry River, all consist of hyalopilitic hypersthene andesite usually containing accessory olivine and sometimes hornblende. They are highly vesicular throughout (Plate 26, fig. 4). A description of their general appearance has been given in the first part of this report. The felspars are the most conspicuous minerals in the hand specimens, some of the larger phenocrysts being more than a third of an inch in length. The pyroxene and olivine formed smaller crystals easily visible without the aid of a lens. The olivine is yellow-green in colour; the matrix is dark grey to black.

The abundant porphyritic felspars are always much zoned, the centres consisting of irregular highly corroded remnants of very basic plagioclase. Around these are successive deposits of felspar varying in composition, more basic and more acid bands often alternating repeatedly. The margins are more acid and more uniform in composition, and are often bounded by good crystalline faces similar to those found in the felspars of the dusts. Albite and Carlsbad twinning are almost universally present, and pericline twinning very frequently. Baveno twins occur, but are rare. Glass cavities with bubbles abound in the felspars, and often have a zonal distribution.

Owing to their perfect freshness these felspars are easily determined by modern optical methods; their specific gravities are not to be relied on because of the complex zoning and the glass enclosures, but fragments from the interior of a large phenocryst sank in a liquid at 2·745 (temperature, 2° C.), indicating 85 per cent. of anorthite in the felspar. The method of determination adopted wherever possible was the measurement of conjugate angles of extinction in Carlsbad-albite twins cut perpendicular to the zone of symmetry of albite twinning. The stereograms of ROSENBUSCH* were used, which differ somewhat in the basic end of the plagioclase series from those of MICHEL LÉVY. Consequently the proportions of anorthite in the felspar are slightly lower than those given by Professor LACROIX, who employed MICHEL LÉVY's diagrams, but the results accord closely if we allow for this. The values given by Professor BECKE in his recent papers on the optical orientation of the plagioclases were also used wherever possible. Determinations by the position of equal illumination in zoned sections, perpendicular to the plane of symmetry of albite twins, proved useful as confirmatory evidence, though not so valuable as conjugate extinctions. Sections perpendicular to the bisectrices were not frequently made use of, as often

---

* ROSENBUSCH, H., "Mikroskopische Physiographie," Band I., Heft 2 (1905). MICHEL LÉVY, A., "Étude sur la Détermination des Feldspaths" (1894, 1896, 1904). BECKE, F., "Die optischen Eigenschaften der Plagioklase," 'Tschermak's Min.-Pet. Mittheil.,' vol. xxv., p. 1 (1906).

much time is required to find satisfactory ones. The optical sign in convergent light is easily observed and often valuable. The microlites of the groundmass were determined by their refractive index as measured against oils and Canada balsam, their maximum extinctions in sections from the zone 001,010 (longitudinal sections), and their extinctions in sections perpendicular to this zone.

The most basic cores of the porphyritic felspars contain about 85 per cent. of anorthite; a great part of the crystal yields extinctions almost identical with those given by Rosenbusch for bytownite (with 75 per cent. of anorthite). The outer margin is more acid than this, having usually about 50 per cent. anorthite, while the external borders may have as low as 40 per cent. A single crystal may thus have zones which vary from the composition of bytownite-anorthite to that of andesine. The groundmass felspars are usually long and narrow, often branched or hollow at their ends, and with few glass enclosures. They belong to andesine, having usually 40 to 35 per cent. of anorthite.

The augite is pale green or greenish brown, and is free from zonal and hour-glass structures. Many of the crystals are idiomorphic, but others have irregular outlines, as if corroded. Repeated twinning on the orthopinacoid may occur. Transverse sections often show good outlines with the pinacoid faces as large or larger than the prisms. The extinction angle $Z : c$ is 45 or 46 degrees, and the axial angle 2E is 110 degrees. The hypersthene is usually idiomorphic, its prisms being four or five times as long as broad. It has eight-sided cross-sections, with the prism faces small, while the pinacoids are large. It is optically negative with axial angle 2V over 60 degrees and the usual pleochroism of this mineral in andesitic rocks:—$Z = c$ green, $Y = b$ reddish brown, $X = a$ paler reddish brown. Parallel growths of augite and hypersthene occur, the augite being external. Both these minerals frequently contain enclosures of glass and magnetite.

Olivine is not always present, but it occurs in more than one-half of the microscopic sections of these bombs. It is never very abundant, and may be regarded as an accessory mineral. In most cases its grains are rounded, though occasionally they present crystalline outlines. Evidently the mineral has suffered corrosion in the period which preceded the eruption, and this accounts for its rounded shapes and the frequency with which it is surrounded by borders of granular hypersthene. The formation of hypersthene in andesites of this sort by corrosion of olivine has been described by many writers, *e.g.*, in the rocks of Martinique. Many of the crystals, however, have no such border, probably because the movements of the still liquid matrix, during the rise of the magma, swept away the hypersthene grains from around the olivine. The two minerals are never in regular parallel growth, and the hypersthene grains have no constant orientation with reference to one another. Agglomerations of hypersthene also occur which probably occupy the place of a former olivine crystal (Plate 26, figs. 1 and 2). It may be mentioned that another feature of these rocks, which is very constant, is the presence of glomero-porphyritic groups of augite, hypersthene, plagioclase and magnetite, very often consisting of granular or imperfect crystals closely packed together.

Dark greenish-brown hornblende is not often seen in sections of these bombs. It is always irregular in shape and corroded; the other ingredients are iron oxides (titaniferous magnetite), pyrites and apatite.

The groundmass is of the hyalopilitic type, consisting of felspar and augite microlites, with magnetite embedded in a dark brown glass. The felspars are mainly andesine, as stated above. The pyroxene is often in long narrow prisms. Hypersthene has been recorded in the groundmass of many of the Martinique rocks, but in St. Vincent, where the microlites are large enough to react clearly on polarised light, they have mostly an oblique extinction, and cross-sections may show twinning on a pinacoidal face; hence they belong to augite. The iron oxides form small octahedra. The glassy base varies somewhat in abundance, and is occasionally nearly free from crystals of the second generation. These rocks are always vesicular, and their steam cavities are empty.

A number of excellent analyses of the dust and bombs of the eruption of the Soufrière in May, 1902, have appeared. Of these we select the following as the most complete. The great similarity is at once apparent. The first analysis probably represents most closely the composition of the magma in the later stages of the eruption. The second analysis contains an abnormally high percentage of water, which leads us to suspect that the specimen was not a recent bomb, but an old and somewhat weathered one. No other analysis of the recent products of the Soufrière or Pelée shows so much combined water, except one which Professor LACROIX[*] suspects for precisely the same reason. Analysis IV. of the dust that fell at Chelston, Barbados, has been criticised by Dr. HILLEBRAND,[†] who doubts whether nickel and cobalt are present in these rocks. Repeated tests, however, both in the laboratory of the Geological Survey of Great Britain and by other analysts to whom samples were sent, confirm the substantial accuracy of the analysis in this respect, though the amount of cobalt and nickel may be very slightly over-estimated. The curious feature of this analysis is that it proves the Barbados dust to contain less silica and alkalies and more magnesia, lime and iron oxide than the average magma of the eruption. In other words, the glass and acid felspars were not deposited in Barbados in normal amount, but were swept past it by the anti-trade wind. Analyses V. and VI. of ash collected 150 miles further away show, as might be expected, exactly the converse. This brings out clearly the sifting action of air currents on clouds of volcanic dust.

Professor LACROIX[‡] has computed that PISANI's analysis shows that the rock, it completely crystallised, would have yielded :—

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[*] 'La Montagne Pelée,' p. 527.

[†] 'National Geog. Mag.,' XIII., p. 299, 1902.

[‡] 'La Montagne Pelée,' p. 599.

Quartz		9·00
Felspars:—	Orthoclase	5·00
	Albite	30·39
	Anorthite	32·15
Pyroxenes		17·98
Magnetite		4·41
Ilmenite		1·52
Apatite		0·34
H_2O		0·34

	I.	II.	III.	IV.	V.	VI.
SiO_2	56·71	55·08	55·64	52·81	57·62	57·75
TiO_2	0·77	0·80	0·98	0·95	0·87	0·70
Al_2O_3	18·80	18·00	18·21	18·79	19·76	17·70
Fe_2O_3	3·12	2·46	3·63	3·28	3·43	2·84
FeO	5·35	4·57	4·83	4·58	3·90	2·73
MnO	—	0·21	0·19	0·28	0·08	—
CoNiO	—	—	—	0·07	—	—
MgO	3·62	3·34	3·48	5·19	1·82	3·51
CaO	8·06	7·74	8·10	9·58	6·25	8·11
BaO	—	—	0·03	—	—	—
Na_2O	3·65	3·45	3·55	3·23	3·79	5·03
K_2O	0·77	0·65	0·58	0·60	0·71	0·94
H_2O	0·11	2·05	0·74	0·37	0·90	1·00
H_2O	—	—	—	—	—	—
P_2O_5	0·08	0·17	0·11	0·15	0·17	tr.
S	—	—	0·04	—	0·11	—
SO_3	—	0·24	—	0·33	—	—
Fe_7S_8	—	0·91	—	—	—	—
Cl	—	—	—	0·14	—	—
	100·95	99·67	100·15	100·35	100·08	100·31

I. Vitreous bomb from the Soufrière (anal. PISANI, cited from LACROIX, 'Montagne Pelée,' p. 598).

II. Lapilli collected at Langley Park, St. Vincent (anal. SCHMELCK, 'Chem. Zeit.,' XXVII., 1903, p. 34).

III. Pumice from St. Vincent collected by Lieutenant PENNY (anal. STEIGER, 'National Geog. Mag.,' XIII., p. 291, 1902).

IV. Dust that fell in Barbados May 8th, 1902 (anal. POLLARD, 'Quart. Jour. Geol. Soc.,' LVIII., p. 368, 1902).

V. Dust that fell on the ship "Coya," 250 miles W.S.W. of St. Vincent (anal. STEIGER, 'National Geog. Mag.,' XIII., p. 291, 1902). (Contains also 0·29 SO_3, 0·20 CaO, 0·08 Na_2O, soluble.)

VI. Lapilli collected at Langley Park, St. Vincent (anal. SCHMELCK, 'Chem. Zeit.,' XXVII., 1903, p. 34).

Old Bombs.

Among the materials washed down by the rivers on both sides of the island were many lapilli and small vesicular bombs, which closely resembled those of the recent eruption, but had a weathered appearance. On section these proved to be hyalopilitic hypersthene andesites very similar to those above described. Probably they were washed out of the ash beds deposited by the eruptions of 1812 and 1718, or even at an earlier date.

Blocks of Older Andesites.

These were easily distinguished from the new bombs by their angular outlines (due to fracture), their less vesicular character, and the traces of weathering or fumarole action they often exhibit. Many of them were 2 feet in diameter, while some were 5 feet long and 4 feet thick. Of these rocks the greater part were hyalopilitic hypersthene andesites with accessory olivine, and differ little from the new bombs of 1902, except in their more solid texture and the general absence of steam cavities. Their groundmass is more crystalline, as a rule, than that of the bombs, owing to their having cooled more slowly, but there is considerable variation in this respect, as some contain much brown glass, while others show very little of it. Many of them are very fresh, and must have been derived from the solidified magma of previous eruptions which occupied the passages leading to the base of the crater, or formed its floor. When the vitreous base is abundant, these rocks have a dark lustrous appearance; when the groundmass is more crystalline they are more grey in colour. All carry phenocrysts of plagioclase, augite, and hypersthene; olivine appears in most of them, and is often surrounded by hypersthene; hornblende is rare. The olivine may contain small dark brown octahedra of chromite or picotite. The hypersthene, when the groundmass is well crystallised, may have narrow borders of augite due to corrosion during the last stages of solidification.

A few of these rocks contain as much olivine as hypersthene, and may be classified as hypersthene basalts (Plate 27, fig. 5). The great resemblance which these old andesites and old bombs present to the new products of the magma of 1902 proves that there has been little change in the nature of the materials emitted by the Soufrière for a very considerable period.

An interesting structural variation presented by some of these andesites is flow-brecciation. In a few of them, although the rocks appear perfectly massive in the band specimens, the porphyritic crystals are broken to fragments (Plate 26, fig. 8). This is especially noticeable in the zoned felspars, as the banding does not then continue round the whole crystal, but stops abruptly at the broken edges. These rocks have a rather crystalline matrix, never a glassy one, and are not vesicular. They show no flow banding, but in the groundmass there are patches of different structure which look almost like enclosed fragments. It is clear that the brecciation took place before the rock was entirely solid, as later deposits have gathered on the broken faces of some of the larger felspars, forming thin continuous marginal zones. At the same time there can be no doubt that the matrix was already partly solid, as the brecciation affects it also. On Montagne Pelée* brecciated rocks are common, and

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* 'La Montagne Pelée,' pp. 513, 514 (1904).

have arisen in several different ways. On the Soufrière they are rare, and as they occur only in scattered blocks among the ashes, there is nothing to indicate in what manner they have originated.

The alterations which the ejected blocks of former lavas have experienced are due to weathering, to fumarole action and propylitisation, and to contact action.

The weathered blocks show changes of a familiar type. Their olivine is replaced by serpentine and carbonates; their hypersthene by bastite; the felspars become cloudy with kaolin and carbonates. In the groundmass the glass is devitrified and stained with limonite and chlorite.

In some cases the groundmass has been replaced extensively by silica. This may be brownish chalcedony showing spherulitic structure, almost the same in appearance as a spherulitic glass, but harder than steel when tested with a knife. The fibres of the spherulites have positive elongation. More common is quartz in small irregular patches replacing the glassy base and enclosing microlites of felspar. This gives these rocks a secondary micropoikilitic structure.

In small cavities in many of these ejected blocks, scales of tridymite are found, and Professor LACROIX has observed cristobalite also in some of them.* It has been pointed out by WEINSCHENK† that tridymite is a fumarole deposit, and indicates that the rocks have been subjected for some time, in the solid condition, to the action of steam at a high temperature. In St. Vincent, as in Martinique, it does not occur in the new bombs of the first eruptions of 1902. Professor LACROIX‡ has made some very interesting observations on its development in the ejecta of Pelée. It began to appear in the vesicular andesites during the winter 1902–03, that is to say, six or eight months after the eruptions had begun. In the materials cast out in 1904, after the dome had stood for some time, tridymite was abundant. It appeared in the enclosed blocks before it was found in the new lava itself.

Rocks of propylite type are also found among the ejected blocks. They are grey or greenish grey masses in which the felspars are often decomposed along certain zones or at their centres, but elsewhere fresh. In these rocks pyrite is common and indicates the operation of sulphurous gases from fumaroles. Chlorite and epidote replace the augite, the hypersthene often yields a pale coloured fibrous mineral with strong double refraction, perhaps iddingsite or a secondary mica. Quartz occurs in some of these rocks; carbonates are scarce. The igneous structures may be perfectly retained, even when the original minerals have entirely disappeared; the whole mass between crossed nicols is nearly isotropic, and apparently consists mainly of kaolin and limonite, but the outlines of all the porphyritic crystals are clearly visible in ordinary light.

The ultimate stages of fumarole decomposition are not well illustrated in

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* 'La Montagne Pelée,' p. 593, 1904.

† 'Die gesteinsbildenden Mineralien,' Edit. I., p. 76, 1901.

‡ *Ibid.*, p. 519.

St. Vincent, as since 1812 the Soufrière crater was occupied by a lake of water and the escape of steam did not take place on a large scale. In Dominica and St. Lucia there are many "Soufrières" discharging sulphurous gases. The crater of Pelée contained a "Soufrière" of this kind, and Professor LACROIX has given a full account of the products of fumarole action in Martinique.

It is rather a remarkable fact that of all the specimens which we collected of older andesitic rocks ejected during the 1902 eruptions only one shows contact alteration. The fresher specimens could not be expected to suffer much change by being again raised to the temperature at which they consolidated. With the weathered rocks it is different, for their secondary minerals would certainly be modified had they been enveloped in the new incandescent lava. Hence we may infer that the ejected blocks above described were mainly the materials which plugged the orifice of the volcano and were cleared out by the rise of the magma.

The specimen which does show contact alteration is a fine grained, dark coloured and banded rock. It consists essentially of dark brown biotite in small scales, rounded or nearly idiomorphic when enclosed in the felspars; hypersthene in minute pleochroic grains; a little augite of similar habit, iron oxides and granular, usually untwinned felspar. The latter is andesine and labradorite; the whole rock has typical hornfels or "pflaster" structure and is indistinctly spotted. Its composition shows that it is igneous, and there can be little doubt that it was originally a fine banded andesitic tuff. In one part the specimen shows larger phenocrysts of bytownite-labradorite felspar, with aggregates of hypersthene and augite (chondritic groups) replacing porphyritic pyroxene. These lie in a fine matrix rich in biotite like that above described. This portion of the specimen seems to be a fragment of andesite in the tuff. The rock is crossed by little veins filled with recrystallised hypersthene. It presents many points of resemblance to the contact-altered andesites of the Cheviots and of Lorne.

Quartz Andesites.

In the ash beds of the 1902 eruptions there are a limited number of andesitic rocks which present some remarkable characters which seem to indicate that they have undergone alteration of an unusual type. These rocks are milky white or pale grey, often with dark patches which represent the ferro-magnesian minerals. Many of them are brecciform; in fact, they look like whitened or bleached tuffs. It is difficult to prepare microscopic sections of them, as they fall to pieces when being mounted.

Under the microscope they prove to be full of quartz which occurs only in the matrix and not as phenocrysts (Plate 26, fig. 5). The original basic felspars of the andesites remain, though small grains of quartz may form along their margins. These felspars often show intense zoning and have much the same characters as those of the andesites and hypersthene basalts. The primary olivine, augite, hypersthene, and hornblende have more or less completely vanished. In their place we have aggregates of dark brown biotite, pale green augite, and hypersthene in small grains which may have parallel orientation, so that they build up skeleton crystals the interstices of which are filled with quartz and felspar. These aggregates do not form good pseudomorphs, and the minerals they represent cannot be identified by their outlines. They are strikingly different, however, from the idiomorphic plagioclase crystals. The process of alteration can be seen in certain large crystals of brown hornblende which are rather common in these slides. The amphibole is reduced to a series of irregular patches (Plate 26, fig. 3), which can be recognised as having belonged to one crystal from their parallel orientation and simultaneous extinctions. The interspaces are filled up by granules of hypersthene and scales of dark brown biotite. These are the only rocks from St. Vincent with the exception of the norites and andesite-hornfelses in which biotite has been observed. In these secondary aggregates pale green augite occurs also, so similar to the hypersthene in colour and mode of growth that it can hardly be distinguished except by its optically positive character and its lack of pleochroism. The hypersthene has a large apparent axial angle, though it is pale green, and is always optically negative. Very little iron oxide occurs in these aggregates.

The groundmass consists of quartz, felspars, hypersthene, tridymite and an isotropic material. The quartz may be in irregular grains; very often, however, it is in perfectly formed double pyramids which, when the matrix is dissolved away, are beautifully sharp. It contains few enclosures, mostly tridymite. The felspars are of many kinds; some are highly zonal and consist mainly of labradorite at their centres with margins of andesine; there are also irregular plates of untwinned alkali felspar which are covered with scales of tridymite. Hypersthene appears in the groundmass as grains and as perfect minute prisms of the usual shape. Iron oxides are practically absent. An isotropic material surrounds and separates all the crystalline minerals of the groundmass in very thin colourless or yellow films. It is dissolved by boiling with caustic potash for some time, and this suggests that it may be a form of colloid silica, but its refractive index is 1·484, but varies slightly, and no kind of opal is known which has so strong refringence. It has also very nearly the same index of refraction as the more acid varieties of andesitic glass which were examined by Professor LACROIX* in Martinique.

It is clear that these rocks have undergone alteration. Their pale colour shows that they contain but little iron; the great abundance of quartz in many of them leads us to suspect that there has been an introduction of silica. The transformation of the hornblende might be ascribed to fusion, or to contact alteration. That the changes have taken place at a high temperature is clear from the occurrence of veins of pyroxene traversing the groundmass, and filling cracks in porphyritic felspar. This shows that after the rock had consolidated there was a formation of augite. They

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* *Op. cit.* p. 511.

have at the same time very little in common with the rocks which have been weathered under atmospheric conditions, or with the propylites. It seems probable that steam, acting at high temperatures and pressures, was the modifying agency. Perhaps these rocks lined fissures beneath the crater through which gases ascended after the eruptions of 1812 and 1718.

In St. Vincent quartz-bearing andesites are rare; in Martinique, where the magma was more acid and the volcanic activity more continuous, they are common. Professor LACROIX has some very interesting notes on these rocks. They did not appear at the first eruptions; but in 1904 the materials produced by the rupture of the dome were full of quartz. He concludes that it arose in those rocks which were situated beneath the surface of the dome, and were affected for a long period by steam emitted from the magma.*

Cordierite Andesites.

Six months after we left St. Vincent Professor LACROIX found two specimens of cordierite-bearing rocks on the Soufrière, one an andesite, the other a variety of quartzite. In our collection there are no cordierite-bearing rocks; probably they were not emitted by the first eruptions; if they were, they must have been very scarce. At Martinique, quartz andesites and cordierite andesites were not obtained till the volcano had been in activity for some months. Some of these rocks seem to bear a close relationship to the quartz andesites above described, but for particulars regarding them we may refer to Professor LACROIX's monograph on Montagne Pelée (p. 597).

Anorthite-Olivine Blocks.

Many crystalline masses, consisting mainly of anorthite and olivine, with augite, hypersthene, and hornblende, occurred among the new ash deposits. They were mostly in a perfectly fresh condition; some, however, must belong to previous eruptions, as their minerals show decomposition. In St. Vincent, several people showed us similar blocks which had been picked up on the Soufrière before 1902; we also saw these blocks in the older tuffs and lavas of the mountain. They occur also in Martinique, St. Kitts, and other islands of the Antilles.

They present a great diversity of appearance in the hand specimens. All are rich in felspar, which is usually milky white rather than glassy and transparent. Olivine in rounded, greenish yellow, or brownish grains, is the next mineral in abundance, and then augite in black crystals which are pale green in thin sections. Dark elongated prisms of hornblende are common in some of these rocks. Of the ferro-magnesian minerals hypersthene is the least frequent.

They have usually the appearance of granular crystalline rocks, the grains ranging in size from half-an-inch downwards. Some contain larger crystals, which give them

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* *Op. cit.*, p. 521.

a porphyritic appearance; others have finer grained bands, which may possibly be veins. We obtained also some blocks rich in long bladed crystals of hornblende (over an inch in length). These are arranged parallel to one another, giving the rock a coarsely gneissose character; or it might be compared to a comby vein with prismatic crystals perpendicular to the boundary walls. There is little olivine in these specimens. Others have a drusy structure with small cavities lined by the terminations of idiomorphic crystals. None of the masses was of large size; specimens over a foot in diameter were scarce. On the other hand, many of the fragments which lay near one another on the ashes were very much alike, as if they were parts of a large block which had been shattered on striking the ground. The great variety in the appearance of these blocks indicates that if they come from a single rock mass situated beneath the volcano, that mass must be very heterogeneous. These blocks were all exceedingly friable, and fell to powder when struck with the hammer, so that thin chips could not be detached from them, a property which will be explained when their microscopic characters are described.

In thin sections none of the minerals have definite crystalline form. The olivine is rounded and often much cracked. The augite is pale green and not dichroic. Its extinction angle Z : *c* is 45 degrees; the optic axial angle 112 degrees. Twinning on 100, simple or repeated, is common. The hypersthene has the usual pleochroism, not very intense: its axial angle 2V is over 60 degrees. The felspar, which is the most abundant constituent, very seldom is zoned. Pericline and albite twinning are both frequent; Carlsbad twins are few. Conjugate extinctions in sections of Carlsbad-albite twins indicate a high percentage of anorthite (85 to 90 per cent.). In convergent light the sections are negative. The specific gravity of the powdered felspar is on an average 2·75. The refractive index and double refraction are both very high. The hornblende is brownish green, fairly deep in colour, and is often in parallel growth with the augite, the two minerals having their prism axes and zones of symmetry parallel. Sometimes the amphibole surrounds the pyroxene; at other times they are intergrown. The pleochroism of the amphibole is X yellow, Y yellow green, Z darker brownish green. Z : *c* about 13 degrees in sections showing vertical emergence of the optic normal. Y = *b*.

All the minerals contain small glass cavities with a fixed bubble; they may also show large enclosures of brown glass. Some of the cavities seem to be empty. Fluid enclosures with mobile bubbles, though they might be expected to occur, were not seen. None of the minerals, though the rocks have plutonic structure, have the dark platy enclosures which produce schiller. As a rule there is no definite zonal or crystallographic arrangement of the glass cavities.

In structure these rocks resemble gabbros and troctolites (Plate 27, figs. 1 and 2). The felspar has partly crystallised after the augite, and may be enclosed in it, but is never enveloped by olivine, which has probably been the earliest of the silicates.

The rocks consist generally of nearly equidimensional grains, fitting together in a perfect mosaic. If regarded as true plutonic rocks they may be classified as gabbros, troctolites, anorthosites, &c. (or seeing that their felspar is anorthite, as allivalites, harrisites, &c.). They have evidently formed under plutonic conditions. Hornblende and olivine are frequent in them, but these minerals are unstable at the levels to which the magma ascends before effusion, and are gradually dissolved. Professor LACROIX has described and figured* fused crystals of hornblende in nodules of this sort from St. Vincent, but we have not met with any in our specimens, where these minerals are always perfectly clear and sound. The felspars of these rocks resemble those of the early central portions of the phenocrysts of the lavas, though somewhat more rich in lime and containing more enclosures. The absence of outer zones of bytownite and labradorite shows that these felspars ceased growing at great depths. All the minerals, however, are like those met with, under certain conditions, in the lavas; hence there can be no doubt that these crystalline rocks are from the same magma, but they have formed at great depths and are more basic in character than the rocks erupted at the surface.

A very interesting structural feature of these rocks is that their minerals are not in perfect contact with one another, but are separated by the thinnest possible films of brown glass (Plate 27, fig. 1). The vitreous material even passes into the cracks and cleavages of the felspars. It seems to enter the original cavities and enlarge them by corroding the surrounding mineral. This glass contains usually only small dusty grains of black magnetite. Near the edges of the specimens the finest veins unite to form thicker ones, which sometimes contain microlites of andesine and labradorite; the glass is consequently similar to that of the hyalopilitic andesite matrix. This makes it probable that the glass veins are an injection of that portion of the magma which was liquid at the time of the eruption; it explains also the absence of zones surrounding the anorthite and intermediate in composition between it and the andesine of the glass. The very friable character of the nodules arises from the presence of these films of brittle glass separating the crystals.

The subjoined analyses show the composition of two crystalline blocks collected in St. Vincent by Professor LACROIX. The second indicates the great abundance of anorthite in some of them; compared with the first, it proves a considerable range in composition in these blocks, though both of them are highly basic. The other three analyses are of anorthite, hypersthene, and hornblende, in a similar block from St. Kitts. Dr. FELS's paper contains also particulars of the crystallographic and optical properties of these minerals. Analysis III. is interesting as proving that the felspar is not absolutely pure anorthite, but corresponds to Ab $12\frac{1}{2}$, An $87\frac{1}{2}$. The felspar of Professor LACROIX's rock must be rather more basic than this. The St. Kitts hypersthene contains 18 per cent. of iron oxides; a sample of hypersthene separated from the rocks of Martinique contained 27·7 per cent.† of iron oxides; if we

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* *Op. cit.*, Plate 26, fig. 6, and p. 542.

† LACROIX, A., *op. cit.*, p. 506.

judge by the optic axial angle, which in this group of minerals varies with the percentage of iron present, the St. Vincent hypersthene is not quite so ferriferous as that of Martinique.

	I.	II.	III.	IV.	V.
SiO_2	47·15	45·0	44·17	50·54	43·26
TiO_2	0·90	0·3	—	—	0·29
Al_2O_3	22·30	32·5	35·06	3·94	13·15
Fe_2O_3	2·22	0·2	—	0·90	2·27
FeO	6·93	3·0	0·58	17·08	10·50
MgO	5·15	0·7	0·57	25·71	15·06
CaO	12·30	17·1	18·84	1·82	12·11
Na_2O	1·81	0·8	1·21	0·79	3·49
K_2O	0·35	0·2	0·43	0·55	0·57
P_2O_5	0·19	—	—	—	—
H_2O	1·00	—	0·59	—	0·21
	100·20	100·8	101·45	101·33	100·91

I. Dioritic enclosure (anorthite-hornblende rock) Chateaubelair (anal. PISANI, cited from LACROIX, 'La Montagne Pelée,' p. 598).

II. Troctolitic enclosure (anorthite-olivine rock), St. Vincent (anal. ARSANDAUX, *ibid.*, p. 598).

III. Anorthite from an anorthite-olivine block from St. Kitts (anal. FELS, 'Zeits. Kryst.,' XXXVII., p. 459, 1903).

IV. Hypersthene from an anorthite-olivine block from St. Kitts (*ibid.*).

V. Hornblende from an anorthite-olivine block from St. Kitts (*ibid.*).

Norites, Quartz-Norites (Andes-Norites).

These are less common than the anorthite-olivine blocks, but are of interest because they represent a type known also in Martinique and some of the other islands and of wide distribution among the volcanoes of the Andean or Pacific facies.* They consist of plagioclase, augite, and hypersthene, and are rather fine grained and holocrystalline, or contain a little glass. Larger phenocrysts of plagioclase may occur, but are scarce. Their felspars, in contrast to those of the anorthite-olivine blocks, are invariably much zoned and are often idiomorphic. They show Carlsbad, albite and pericline twinning in great perfection. The centres of different crystals proved to contain 80, 75, and 60 per cent. of anorthite; bytownite is evidently the prevailing type. These centres are corroded and surrounded by more acid zones succeeding one another in great numbers; more and less acid bands may alternate repeatedly. The margins are often andesine with 35 per cent. anorthite, but oligoclase (20 per cent.

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* ROSENBUSCH, H., 'Mikroskopische Physiographie,' B. II., p. 292 (1907); HÖGBOM, A. G., "Zur Petrographie der Kleinen Antillen," 'Bull. Geol. Inst. Upsala,' vol. vi., p. 214 (1905).

anorthite) forms the outer borders of some crystals. Glass cavities are frequent (Plate 27, fig. 3). In all their features these felspars resemble the phenocrysts of the andesites.

Augite and hypersthene are about equally common, the former sometimes euhedral, but often anhedral; the latter always occurs in long prisms similar in shape to those of the lavas. The augite has a green colour and simple or repeated twinning on 100. The hypersthene is pleochroic in the usual tints; one section gave an optic axial angle 2E = 132 degrees (which corresponds to 2V = 65 degrees). Parallel growths between the pyroxenes occur as in the andesites; they also contain glass enclosures. A few scales of dark brown biotite are sometimes present. Olivine occurs in several of these norites, but is scarce and is always surrounded by corrosion borders of hypersthene (Plate 26, fig. 1). The other ingredients are magnetite and apatite.

In all these rocks there are traces of a matrix between the larger crystals, though this is not abundant. In some it is felspathic and consists of small imperfect crystals of andesine. In others it is a brown glass, very scanty in amount. This glass resembles that of the enclosures and does not seem to be a later injection, as in the anorthite-olivine nodules. Most of these rocks, however, contain a small amount of micropegmatite (Plate 26, fig. 7), which serves as a groundmass and forms aureoles around the felspars. The latter then have borders of oligoclase; the felspar of the micropegmatite is untwinned alkali felspar with lower refractive indices than those of the quartz.

These rocks approach closely in composition and in the peculiarities of their minerals to the effusive andesites and differ greatly from the anorthite-olivine nodules. The scarcity of olivine, the zonal structure of the felspars, and the presence of glassy base in some of them proves that they crystallised at intermediate depths and pressures. They represent the rocks which would have been produced had the andesitic magma solidified without forcing its way to the surface.

Sedimentary Rocks.

Calc-silicate Hornfelses.—The sedimentary rocks ejected by the eruptions of May, 1902, all occurred in small fragments among the ash and were much contact-altered. The commonest were fine grained, pale green or greyish-green calc-silicate rocks. In all probability they represent sedimentary beds which lie beneath the volcano. The hand specimens are often banded, apparently owing to original bedding; often they are crossed by irregular veins, and they may show spots due to local aggregation of wollastonite, augite, or other minerals. Similar blocks had been thrown out by previous eruptions, and as they are fine grained and tough were used by the Caribs in the manufacture of stone implements.

These rocks contain little carbonates and most have originally been impure siliceous and argillaceous limestones. Some consist mainly of wollastonite, with granular augite and sphene; in others lime-felspar is common, while a few contain small rounded grains of quartz. The absence of hornblende, garnet, vesuvianite, and epidote is rather striking.

The wollastonite, which is the most important mineral, forms plates, fibres, and irregular blades. Sometimes it shows traces of idiomorphism, being elongated parallel to the *b* axis. Very often its fibres are sub-radiate, or have a tendency to spherulitic or stellate groupings. The augite is dark green, sometimes brownish green, and forms only small grains which rarely exhibit crystalline faces. The felspar, also, is anhedral as a rule. It shows albite twinning, more rarely Carlsbad and pericline twinning, and belongs to the basic end of the plagioclase series, being near anorthite in composition. Quartz is rare and occurs only as rounded grains. Granular sphene is always present, but never well crystallised.

The green veins which traverse these rocks are mainly augite; the white patches consist of wollastonite and felspar, but the rocks show little uniformity in structure or in the shape and size of their component minerals.

Where anorthite is abundant it has a tendency to idiomorphism, and its crystals are frequently bounded in part by good crystalline faces (Plate 27, fig. 4). The matrix is then wollastonite, augite, and smaller grains of felspar. The large felspars enclose wollastonite, augite, and the other minerals of the rock. The porphyritic crystals give rise to a structure somewhat resembling those of igneous rocks. Professor LACROIX has noted the same phenomenon in the calc-silicate hornfelses of St. Vincent.

Quartzites, Baked Sandstones.—We obtained also a few fine-grained contact-altered rocks consisting mainly of quartz. They may have been sandstones or siliceous portions of the underlying sedimentary beds, or perhaps secondary deposits of quartz among the igneous rocks.

Albite Rock.—The most peculiar of these rocks is a small pale-coloured fragment which proved in microscopic section to consist of albite and pleochroic green augite (ægirine augite). In the calc-silicate hornfelses the pyroxene sometimes has a weak pleochroism; in the granular augite of this rock it is quite strong and ranges from yellow to dark green. The albite forms long prisms, not perfectly idiomorphic, but with irregular or indented edges. A little quartz occurs among the felspars. There are no phenocrysts. The origin of this rock is obscure; it is unique in our collections, and no similar ejecta have been found in Martinique. As its pyroxene resembles that of some of the calc-silicate hornfelses, we have placed it with them.

THE OLDER IGNEOUS ROCKS OF ST. VINCENT.

Our collections do not include a large number of specimens of the older igneous rocks of St. Vincent, but they have been supplemented by a series which Professor LACROIX sent us, and these enable us to show what are the main petrographical features of the island. Professor BERGEAT has grouped the rocks which were collected by Professor SAPPER[*] as felspar basalts, hypersthene-bearing basalts, basalts, olivine augite andesites, hypersthene andesite, hypersthene augite andesite, and hornblende pyroxene andesite. Professor LACROIX[†] has classified his specimens as andesites, andesilabradorites and labradorites with augite and hypersthene, and basalts. Recognising that they all belong to one series and are linked together by intermediate types, we shall describe them as hypersthene andesites (with accessory olivine and hornblende), hypersthene basalts (with both olivine and hypersthene) and olivine basalts; this terminology is more in accordance with the nomenclature current in Great Britain.

The *hypersthene andesites*, except that they are more or less decomposed, bear a strong resemblance to those ejected by the Soufrière during 1902. They are all porphyritic, the minerals of the first generation being plagioclase, augite, and hypersthene, while the groundmass consists of augite, plagioclase, and iron oxides. Magnetite and apatite are constantly present; hornblende occurs in a few specimens, as in the recent bombs of the Soufrière. Olivine is more common, and is often surrounded by a resorption border of hypersthene. Small nodules or glomero-porphyritic groups of hypersthene are common in these rocks, and represent the final stages of resorption of olivine (Plate 26, fig. 2). They often contain branching growths of magnetite at their centres, showing that part of the iron oxides was rejected in the transmutation from olivine to hypersthene. The hypersthene is usually idiomorphic, but when the matrix is comparatively well crystallised, a zone of augite surrounds it, and has probably formed by corrosion of the hypersthene during the last stages of crystallisation of the groundmass. The porphyritic felspars are much zoned, consisting of bytownite (80 per cent. anorthite) at their centres, while their margins are acid labradorite and andesine. The groundmass felspars are andesine (about 40 per cent. An), and occur as small elongated laths; the augite of the second generation is granular and usually anhedral. Most of these rocks contain little glassy base, and are far less rich in this substance than the recent bombs of the Soufrière, but had the latter cooled slowly as in a lava flow, they would have very much the same structure as many of the older andesites.

As indicated by the ejected blocks of the 1902 eruption, there is much hypersthene andesite in the Soufrière, though hypersthene basalts occur there also, and Professor BERGEAT[‡] mentions two olivine basalts from the Black Ridge on the mountain. Hypersthene andesites are exposed at Morne Ronde, Larikai, and Baleine, and occur also at Cumberland, north of Chateaubelair.

The *hypersthene basalts* are richer in olivine than the hypersthene andesites, but contain less hypersthene (Plate 27, fig. 5). They may be defined as consisting of plagioclase, augite, olivine and hypersthene, with the last two minerals in nearly

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[*] KARL SAPPER, 'In den Vulkangebieten Mittelamerikas und Westindiens,' p. 194 (1905).

[†] *Op. cit.*, p. 592.

[‡] In KARL SAPPER, 'In den Vulkangebieten Mittelamerikas und Westindiens,' p. 194 (1905).

equal proportions. The olivine shows resorption with formation of hypersthene; the latter is often partly replaced by augite. The porphyritic structure of the andesites is repeated in this group. The large felspars are highly zonal, and have centres of bytownite (75 to 85 per cent. anorthite), while the margins are labradorite (about 50 per cent. anorthite). There is rarely much glass in the matrix of these rocks, and in this respect they show affinities to the basalts. Hypersthene basalts occur in small numbers among the ejected blocks of the Soufrière, and are found also at Chateaubelair, Cumberland, Buccament, and other portions of the island. According to Professor BERGEAT the Somma of the Soufrière contains rocks of this type.

The *olivine basalts* consist of plagioclase, augite, and olivine. Hypersthene is rare or absent and hornblende is not known to occur in them. Coarsely porphyritic and finely porphyritic types occur. Some carry large phenocrysts of felspar; others contain only porphyritic augite and olivine. Many of the latter group are very rich in olivine (Plate 27, fig. 6), which acquires a rusty brown colour as it weathers and ultimately passes into serpentine. The large felspar phenocrysts are much zoned, though not so markedly as those of the andesites. Their centres are similar to those of the felspars in the hypersthene basalts; the borders are labradorite and in the groundmass the small elongated microliths have labradorite centres with outer zones of andesine. Olivine may occur as small crystals of the second generation in the groundmass. The augite is less green and more brown in colour than in the andesites. Traces of a vitreous base are to be seen in some basalts near Cumberland, but this is not common. Tridymite may occur in cracks and cavities in the groundmass.

Basalts have been described from Chateaubelair Point by Professor LACROIX. He compares them with the rock of Ramiers Island in Martinique. Professor BERGEAT identified specimens from Buccament and the Soufrière. They occur also at Barroualee, Cumberland, Calliaqua, and Kingstown. Many of the largest lava flows appear to belong to this group.

Two analyses (cited from Professor LACROIX) are given below, one of a hypersthene basalt, the other of an olivine basalt from St. Vincent. They show very well the decrease in silica and the alkalies, accompanied by an increase in lime and still greater increase in magnesia, which are to be expected from the mineralogical constitution of these rocks. Compared with the analyses of recent bombs, already given, they prove that the hyalopilitic hypersthene andesites recently erupted are the most acid lavas known to occur in the island.

The petrography of St. Vincent, so far as is known, is less varied than that of Martinique, Grenada, and Dominica. Hornblende andesites, dacites, trachytes, and rhyolites apparently do not occur, and there is no evidence that plutonic rocks are anywhere exposed at the surface. The absence of the more acid types which are found in Martinique and Dominica is the most striking feature of the petrography.

	I.	II.
SiO_2	53·51	48·71
TiO_2	1·06	1·08
Al_2O_3	18·90	18·40
Fe_2O_3	3·37	3·70
FeO	5·70	5·33
MgO	4·38	10·30
CaO	9·15	10·11
Na_2O	3·13	2·34
K_2O	0·51	0·43
P_2O_5	tr.	0·06
H_2O	0·12	0·25
	99·79	100·71

I. Hypersthene basalt (*labradorite à hypersthène*) from the Somma of the Soufrière (anal. PISANI).*
II. Olivine basalt from Chateaubelair Point (anal. PISANI).*

All the rocks are basic types of andesite and basalts. Hypersthene and olivine are the characteristic minerals with highly zonal crystals of plagioclase.

During the recent eruptions in Martinique and St. Vincent, in spite of all variations the more basic character of the ejecta in the southern island has been maintained throughout. Perhaps for this reason the outbursts have been fewer and less spasmodic; other consequences are the comparative scarcity of pumice, the absence of bread-crust bombs which were partly solid when they struck the ground, and the non-appearance of quartz in the new St. Vincent andesites. After the emergence of the dome in the crater of Pelée, many of the ejected blocks had a quartzose groundmass.

The greater viscosity of the magma in Martinique led to the extrusion of the lava as a high pillar which rose from the crater. No counterpart of this is known on the Soufrière, where the floor of the crater is now almost exactly at the same level as before the 1902 eruptions. The more basic character of the rocks of the Soufrière probably accounts also for the greater abundance of anorthite-olivine blocks.

In spite of these differences there is a great similarity between the products of the eruptions in Martinique and St. Vincent. Representatives of every type of rock described here† have been obtained by the French geologists from the active or extinct volcanoes of Martinique.

The material of the eruption of 1902 is the most acid which has been found in St. Vincent, where also hypersthene andesites are most common in the Soufrière at the north end of the island. For a prolonged period this volcano has erupted only andesitic materials. In its earlier stages, when flows of lava were more common,

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* LACROIX, A., 'La Montagne Pelée,' p. 598.

† With the exception of the albite rock described on p. 322

hypersthene basalts were emitted. The latest eruptions have been entirely of the spasmodic type, the effusive having given place to the explosive phase. This may not be without significance, especially seeing that most of the great explosive outbursts of recent years, Krakatoa, Bandaisan, Tarawera, Santa Maria, &c., have been produced by andesitic magmas. This may be explained by supposing that a magma of this nature retains its steam in solution till it is on the point of solidification, and then releases it suddenly with great violence.

The Dusts that fell in Barbados in 1812, October 1902, and March, 1903.

By the kindness of Sir Daniel Morris and of the Rev. N. B. Watson, vicar of St. Martin's, Barbados, we have received specimens of all the dust-falls of volcanic ash from St. Vincent, which are known to have taken place at Barbados. Their dates are May 1, 1812, May 7, 1902, October 16, 1902, and March 22, 1903. All consist of the same minerals and have very much the same appearance. They differ slightly in colour and in coarseness. The dust of 1812 is distinctly paler brown than that of May 7, 1902, and that of March 22, 1903, is rather darker. The dust of October 16, 1902, is very fine and of a grey colour, resembling in this respect the finer dusts from Montagne Pelée in Martinique. It is the lightest coloured of all the Soufrière dusts which have fallen in Barbados.

Samples of these dusts were passed through sieves having 30, 60, and 90 meshes to the inch. This gives a rough test of the size of the component grains. The meshes of these sieves were measured under the microscope and proved to have the average diameters stated in the last column of the table.

Meshes to 1 inch.	1812.	May 7, 1902.	October 16, 1902.	March 22, 1903.	
	per cent.	per cent.	per cent.	per cent.	mm.
30 retains . . .	0·17	0	—	0·0	>0·73
60 ,, . . .	11·76	5	—	0·1	>0·31
90 ,, . . .	7·97	26	1·8	0·2	>0·19
90 passes . . .	80·10	69	98·2	99·7	—

These show that the 1812 dust contained most coarse particles. Many of these were small vesicular pieces of pumice, very light, and hence likely to be transported to a great distance. The dust of May, 1902, is coarser than any other Barbados dust of the recent eruptions, probably because it had been projected into the air with greater violence and to a greater height; hence, when the cloud passed eastwards over Barbados, it still retained a larger proportion of the coarser particles.

The minerals of these dusts are the same as those of the May eruptions of 1902. All contain plagioclase felspars, augite, hypersthene, and olivine. Hornblende was seen only in the dust of May, 1902. Glassy material, more or less devitrified by crystallisation, magnetite and apatite also are present in all the samples. There are, however, points by which these dusts can be distinguished from one another. The 1812 dust is by far the richest in brown glass,[*] often very free from microlites; it occurs largely as minute rounded spongy lapilli. The dust of October, 1902, which is very fine and pale coloured, is also rich in glass, which occurs as minute broken splinters. In this dust also broken felspars are very common, which circumstance probably accounts for the greyish colour of the samples. Olivine is comparatively infrequent. The dust of March, 1903,[†] is also fine grained, but is very dark in colour, being deep brown. This dust contains more olivine than any other of the specimens examined, and its crystals are often coated with very dark films of glass. Professor LONGFIELD SMITH[‡][§] has noted that this dust is richer in ferromagnesian

ANALYSES of Volcanic Dusts from St. Vincent, which fell in Barbados.

	I.	II.	III.
SiO_2	52·81	50·722	51·523
TiO_2	0·95	1·150	1·000
Al_2O_3	18·79	12·550	21·648
Fe_2O_3	3·28	9·484	6·372
FeO	4·58	4·676	
MnO	0·28	0·450	—
$(CoNi)O$	0·07	—	—
CaO	9·58	10·100	10·000
MgO	5·19	5·911	4·716
K_2O	0·60	0·531	0·675
Na_2O	3·23	3·451	3·551
P_2O_5	0·15	0·192	0·141
SO_3	0·33	0·108	0·124
Cl	0·14	—	—
H_2O − 105° C.	0·20	0·130	0·190
H_2O + 105° C.	0·17	0·545	0·060
	100·35	100·000	100·000

I. Dust that fell on Barbados, May 7 and 8, 1902 (anal. Dr. W. POLLARD, 'Quart. Journ. Geol. Soc.,' LVIII., p. 369, 1902).

II. Dust that fell on Barbados, March 22, 1903 (anal. Professor D'ALBUQUERQUE, 'West Indian Bulletin,' vol. IV., p. 98, 1903).

III. Dust that fell on Barbados, May 7 and 8, 1902 (anal. Professor D'ALBUQUERQUE, 'West Indian Bulletin,' vol. III., p. 283, 1902).

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[*] PRIOR, T. G., 'Quart. Journ. Geol. Soc.,' LVIII., p. 370 (1902).

[†] BONNEY, T. G., "Notes on March Dust from the Soufrière," 'Nature,' vol. 67, p. 584 (1903).

[‡] SMITH, LONGFIELD, "Volcanic Eruptions in the West Indies," 'West Indian Bulletin,' vol. III., p. 271, 1902).

[§] Anon., "Notes on fall of Volcanic Dust at Barbados, March 22, 1903," 'West Indian Bulletin,' vol. IV., p. 91 (1903).

minerals than any of the others, and that augite is the predominant pyroxene. If we compare the analyses given below, it is clear that the 1903 dust is more like a hypersthene basalt in composition. The May dust of 1902 resembles a hypersthene andesite. Yet as the 1903 eruption was a small one compared with that of May, 1902, it might have been expected that a larger proportion of the heavy particles would have subsided before the cloud reached Barbados. From this it seems clear that there was a slight change in the composition of the magma erupted by the Soufrière during the 12 months for which it had been in activity, and that the last emissions were more basic than the earlier. As Professor D'ALBUQUERQUE's analysis is not stated in exactly the same way as Dr. POLLARD's, we give also the results of his examination of the dust of May 7 and 8, 1902, for comparison; it shows the more acid character of the latter clearly.

APPENDIX.

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Of the Principal Books and Papers Relating to the Eruptions of 1902 and 1903 in St. Vincent.

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DESCRIPTION OF PLATES.

PLATE 26.

Fig. 1. *Norite*, Wallibu, St. Vincent (polarised light, magnified 55 diameters).

Shows a crystal of olivine surrounded by a corrosion border of hypersthene.

Fig, 2. *Hypersthene basalt*, Calliaqua, St. Vincent (magnified 24 diameters).

A hypersthene cluster full of spongy magnetite, the product of the resorption of olivine.

Fig. 3. *Quartz andesite*, Soufrière, St. Vincent (magnified 47 diameters).

Part of a large crystal of hornblende which is being replaced by hypersthene, biotite and felspar. The scaly biotite is very dark; the hypersthene and felspar are pale coloured. The hornblende (dark) occurs only as islands surrounded by the other minerals.

Fig. 4. *Bomb* (*hypersthene andesite*) of the May eruptions, 1902, Wallibu, St. Vincent (magnified 36 diameters).

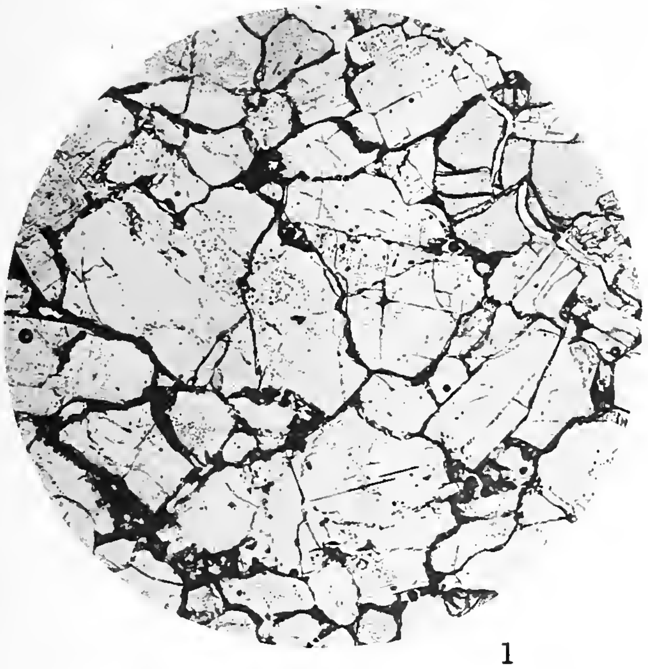
The photograph shows phenocrysts of augite, hypersthene, and plagioclase felspar in a vesicular, semi-vitreous groundmass.

Fig. 5. *Quartz andesite*, Soufrière, St. Vincent (magnified 47 diameters; polarised light).

Highly zoned phenocrysts of plagioclase felspar lie in a matrix full of small brightly polarising grains of quartz.

Fig. 6. *Hypersthene andesite*, Soufrière, St. Vincent (magnified 24 diameters; polarised light).

Below the centre of the photograph there is an idiomorphic cross-section of hypersthene so placed that it is extinguished; around it there is a narrow border composed of granular augite.



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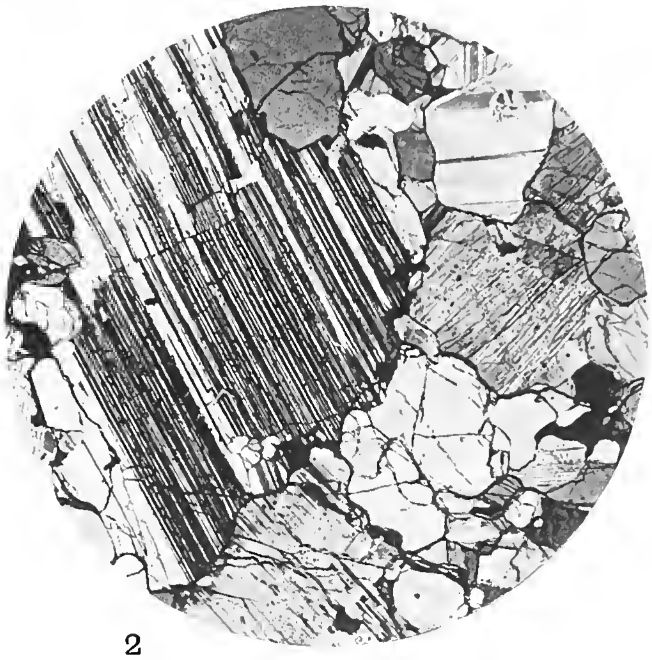

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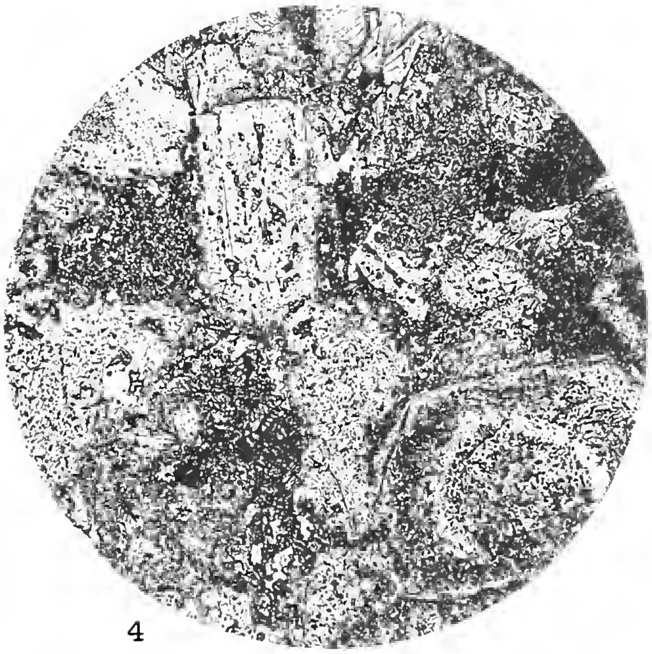

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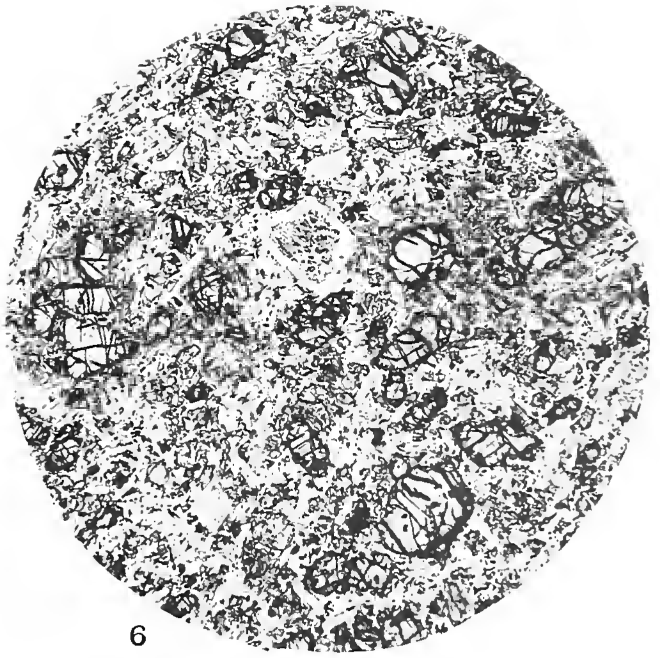

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SERIES A, VOL. 208, pp. 333–347.
[PLATES 28–29.]

THE CONSTITUTION OF THE ELECTRIC SPARK

BY

T. ROYDS, M.Sc.,
BEYER FELLOW OF THE MANCHESTER UNIVERSITY.

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IX. *The Constitution of the Electric Spark.*

By T. Royds, *M.Sc.*, *Beyer Fellow of the Manchester University.*

Communicated by Professor A. Schuster, *F.R.S.*

Received January 29,—Read February 13, 1908.

[Plates 28–29.]

1. *Previous Experiments.*—In the year 1899 Professor Schuster and Dr. Hemsalech* published the results of their experiments on the Constitution of the Electric Spark. On a slit parallel to the spark they formed an image of a spark produced between metal electrodes by a Wimshurst machine and photographed the light passing through the slit, both directly and after analysis by a prism, on a moving film in the focal plane of the camera lens, the direction of motion of the film being at right angles to the direction of the slit. A summary of their results is given below :—

(1.) In the photographs on the moving film the lines in the spectrum which are due to the metallic vapour were inclined, whilst the air lines were straight.
(2.) They regarded the inclination of the lines as an indication of the velocity of propagation of the metallic vapour, and did not discuss any possibilities of the propagation of luminosity through vapour which may be, as a whole, stationary.
(3.) Different lines in the spectrum had different inclinations. This was most marked in the bismuth spectrum.
(4.) The lighter metals had a greater velocity than the heavier metals.
(5.) The calcium lines H and K, due to impurities in the silver electrodes, became luminous first in the centre of the gap, and were propagated towards the electrodes.
(6.) Of the vibrations excited by the discharge those of some periods are intense and of short duration, whilst those of other periods are too faint to show in the moving photograph, but are visible in the stationary one because the vibration persists some time.

---

* Schuster and Hemsalech, 'Phil. Trans.,' A, vol. 193, p. 189 (1899).

2. *Aim of the Present Research.*—Professor SCHUSTER suggested that I should repeat and continue the experiments done by himself and Dr. HEMSALECH. It was hoped to obtain photographs with greater dispersion, greater resolving power, and improved definition, which would remove the doubts expressed by other observers regarding the interpretation of the photographs, and would elucidate still further the constitution of the spark.

3. *Apparatus Employed.*—The arrangement ot the apparatus was substantially the same as that used by SCHUSTER and HEMSALECH, except that two prisms were used instead of one. The prisms, which were kindly lent by Dr. R. S. HUTTON for this research, had each an angle of 60 degrees and a base of 5 centims. The glass is a medium flint, of high transparency to the ultraviolet. The prisms were tested separately by observing the sodium D lines produced by a sodium bead in the Bunsen flame. The definition appeared to be perfect, and was not improved by allowing light to pass through only a narrow portion of the prism. With these prisms and the same lenses as were used in the previous work the extent of the spectrum from F to H is 2 centims.

The optical system was adjusted as described in the paper referred to, and the prisms placed in the position of minimum deviation for about λ 4200, the centre of the region to be photographed. The same method of focussing the spectrum on the photographic film has been adopted. The photographic film is carried on the same disc as used by the earlier experimenters, and can be rotated by a motor at speeds up to 160 revolutions per second. The speed of the disc is given by that of the motor read by a direct-reading speed-indicator by Elliot Bros., which has been tested and found accurate.

The sparks were obtained between metallic electrodes from a condenser charged by means of a large Wimshurst machine capable of producing, without condensers, sparks 12 inches long. The best form for the electrodes is conical. Their surfaces were prepared with fine emery cloth, and finally polished by rubbing with wash-leather to remove small projections which would cause preliminary discharges before the condensers were fully charged, or which might affect the results on account of the distribution of the electric force near them. This preparation of the electrodes, however, probably introduces the calcium lines H and K into the spectrum. The condensers consist of plates of glass coated with tinfoil, connected in parallel with each other. The total capacity is 0·0306 mfd. They could be divided so as to obtain capacities of 0·0206 and 0·0103 mfd., roughly two-thirds and one-third of the total capacity.

The improvement of the definition of the photographs reproduced in this paper over those of SCHUSTER and HEMSALECH is due to the improved optical quality of the prisms used and the greater care taken in preventing a backward or forward displacement of the rotating disc.

4. *Measurement of the Photographs.*—If both electrodes are of the same material,

so that the lines which appear at both the top and bottom of the spectrum can be measured and the means taken, SCHUSTER and HEMSALECH showed that the velocity of the vapour between two points is equal to

$$\mathrm{K}v\,\frac{y_2-y_1}{x_2-x_1},$$

where

K is the reciprocal of the magnification of the system (= 1·16);
v is the velocity of the film at the centre of the spectrum;
x_1, x_2, the co-ordinates of the points measured parallel to the spectrum;
y_1, y_2, the co-ordinates of the points measured at right angles to the spectrum.

Even if the line can only be measured at either the top or the bottom, this expression may generally still be used, the differences from the more accurate one being less than the errors of experiment. If, however, it should be required to calculate velocities from the more accurate formula of SCHUSTER and HEMSALECH, it will be necessary to know the distance of any line in the spectrum from a vertical through the centre of the disc. This has been obtained by measuring on the disc itself the distance of a vertical through the centre of the disc from where the air line λ 5004 falls on the disc. From this, the distance for any line in the spectrum can be found.

Method of Making the Measurements.—A number of fine lines were drawn parallel to each other, at equal distances of about 8 millims., on a sheet of paper, and reduced to the necessary size by photographing on a glass plate. In this way rulings have been made whose spaces were 0·0503 centim. and 0·0200 centim.

The photograph of the spectrum was placed flat on the ruling with the two emulsions together, and clamped on the travelling microscope stage of KAYSER'S measuring machine, the pitch of whose screw is $\frac{1}{3}$ millim. The stage is moved by turning the screw until the vertical wires in the eye-piece are on the point where a streamer intersects a line of the ruling, and the reading of the screw head then recorded. Thus the ruling gives the y readings, and the screw the x readings.

The x readings have to be corrected for the curvature of the spectral lines which is introduced by the use of prisms.

It is necessary that the spectral lines and the vertical wires in the eye-piece should both be at right angles to the direction of travel of the stage, and the lines of the ruling parallel to this direction. Since the lines in the stationary photograph are finer than the air lines in the rotating one, the adjustments are first carried out by means of the stationary photograph. The photograph is clamped to the ruling with spectrum parallel to the lines of the ruling. The whole is then adjusted on the stage until a point in the eye-piece remains on a line of the ruling as the screw turns. The ruling and the spectrum are then parallel to the direction in which the microscope stage travels and the spectral lines at right angles to it. The wires in the eye-piece are then rotated until they pass through the ends of a fine spectral line. A rotating photograph being substituted for the stationary one and the lines of the ruling again set parallel to the direction of travel of the microscope stage, readings can now be made. Adjusting by means of the stationary photograph also possesses the advantage that it is not necessary to assume that the air lines appear simultaneously at the top and bottom of the spectrum.

Latterly the velocities have been obtained by taking enlargements (about 10 times) on bromide paper of the negatives and measuring these with the millimeter scale. The accuracy with which this can be done is, except for short lines indicating a large velocity, not so great as the error of experiment. Moreover, more detail can be seen in the enlargements than in the microscope even when using small powers, and the measurements can be made more rapidly.

Accurate measurements of wave-length are not required, the finer air lines and a few well-known metallic lines were used to draw a dispersion curve from which any line could be identified. Measurements of the distances of the metallic lines from the air lines have, however, been made on the stationary photographs for comparison with the moving.

5. *The Photographs.*—In most cases the photographs have been taken in the following manner. A spark was made with the film stationary. The motor having been started, the handle of the Wimshurst was turned by an assistant until about six sparks had passed. The interval between successive sparks would be about a quarter of a minute. Occasionally the stationary photograph was taken last.

In all the photographs reproduced in the plates, the spark length was 8 millims., the upper electrode being the initially positive one. In each case the capacity of the circuit was 0·0306 mfd., and the self-induction that of the leads, the period of the oscillations being $3·8 \times 10^{-6}$ second. The speeds of the film at the centre of the spectrum were about 90 metres per second.

It was soon found that the most regular structure in the moving photograph was given by the lead lines λλ 4387, 4245, and the bismuth line λ 4260. The lead spectrum photographed on the moving film is shown enlarged about six times in Plate 28, fig. 2, and the bismuth spectrum in Plate 28, fig. 4, together with the photographs on the stationary film.

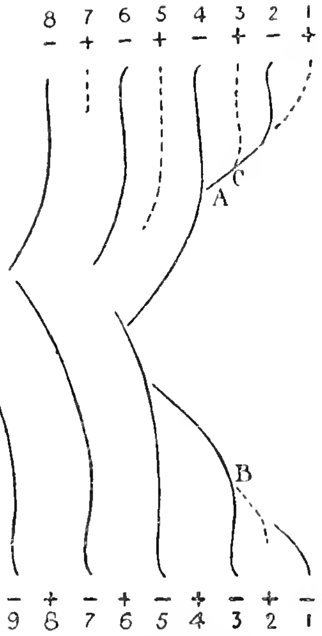
There is a slight loss in the definition of the air lines in the moving photographs due to a broadening caused by the air particles remaining luminous for a short time. The air lines shoot straight across the spark gap, whilst the metallic lines are obliquely inclined at each electrode. The inclination of the metallic lines indicates the velocity with which the particles of metallic vapour travel away from the electrodes. The discharge is oscillating, the period of the oscillations being large enough for them to be separated in the photograph.

Let us examine in detail the photograph of the two lead lines, λλ 4387, 4245, shown enlarged about ten times in Plate 29, fig. 5. It is noticed that the streamers start alternately at the top and bottom of the spectrum. However, in the case of the intense short lines of the spectrum there generally appear, in addition to these, fainter streamers, which are simultaneous with the strong ones at the opposite electrode; the faint streamers rarely appear in the two lead lines shown and long lines in general. By comparing the positions of the commencements of the streamers relative to the air lines with the positions of the spectral lines in the stationary photograph we can measure the time from the passage of the air discharge when the streamers start, and find the sign of the potential of the electrode from which they start if we know the polarity of the electrodes before the spark passes. It is found that the first streamer starts at both electrodes practically simultaneously with the air lines. The intense streamers come from the electrodes when negative, and those coming from the electrodes when the potential is positive are faint or absent, except for the first streamer from the initially positive electrode, which is always quite strong.

Schuster and Hemsalech discovered that all lines of the same spectrum did not indicate the same velocity. The measurements show that there are, as a rule, two velocities. The long spark lines form one class having the smaller velocity, the short lines comprising the second class with the greater velocity. Only in the case of mercury is the line with greater velocity a long one.

Let us examine a typical case of a line of the first class, *e.g.* λλ 4387, 4245 of the lead spectrum, and λ 4260 of the bismuth spectrum shown in Plate 29, fig. 6. Consider only the streamers from one electrode. The first streamer does not reach more than about 1 millim. (in the actual spark) towards the middle of the gap, the second reaches farther and the third still farther, and so on until the streamers from the other electrode are met, beyond which they do not as a rule pass. The first streamer is almost vertical at its commencement and becomes more inclined as it extends farther out. The first streamer is followed by another intense streamer from the same electrode when the potential becomes negative (for when the electrode is positive the streamer is either faint or quite invisible), *i.e.*, after a half period if the electrode considered is the initially positive one (the upper electrode in the photographs), or after a whole period if the electrode is the initially negative one. This second streamer begins at the electrode and is practically vertical throughout its length until it overtakes the first streamer, when it bends over more or less suddenly into a line continuous with the first streamer. The third streamer behaves similarly, bending over when it overtakes the second. In the majority of cases of lead and bismuth photographs the third streamer reaches to the middle of the gap. It is thus seen that the first streamer together with the latter portions of the successive streamers form a kind of envelope reaching from the electrode to the middle of the gap. The fourth and following streamers are similar to their predecessors. A careful examination shows that the streamers after the first have near their bases for a length of about $\frac{1}{4}$ millim. (in the actual spark) a large inclination which would indicate a velocity of about 170 met./sec. and have in this short length become less intense. The streamer now makes a sharp bend and immediately becomes practically vertical, growing more intense as it advances. We notice that this sudden bend at the commencement of the streamers becomes less pronounced as the order of the streamers increases, and that the inclination of the streamers is becoming less steep than the steep portions of the first three or four.

[*Added, April* 3.—An enlarged drawing of the lead line λ 4386 of fig. 5 is shown in the accompanying figure, the lines representing the first edges of the streamers.



Drawing of λ 4387 (Pb) of fig. 5, Plate 29.

The instantaneous polarity of the electrodes is marked and the streamers from electrodes when positive are shown dotted. The first edges of the 4th and 6th positive streamers are not visible.]

We have also to consider the second class of line, which comprises the short lines of the spectrum. An example is λ 4561 of the bismuth spectrum shown in Plate 29, fig. 7. These lines have a very high velocity, for the first streamer is nearly vertical. Streamers proceed from the electrode both when positive and when negative, although stronger in the latter case. The commencement of the streamers is not bent as was noted in the first class of lines, and the first streamer is never overtaken by a following one. Although the measurements of velocity are most uncertain near the electrodes, yet this greater velocity is real and not due to uncertainty of measurement. On account of the width of the short lines becoming smaller at their tips in the stationary photograph, the readings have been taken on the most intense portion of their streamers; any error due to this cannot be great, for the lines are almost as sharp as in the stationary photograph.

6. *Interpretation of the Envelope.*—We now attempt the problem of finding the velocity of the metallic vapour. So long as the vapour first produced remains luminous it must indicate the velocity with which it is travelling, *i.e.*, the first

streamer throughout its length shows the velocity of the vapour. Before the first streamer has completely died away, having reached only a short distance from the electrodes, it is met by a following streamer. If new vapour has been produced by the oscillation causing this streamer, it will, like the metal first vaporised, indicate, so long as it remains luminous, the velocity with which it is travelling from the electrode where it is produced. Also, unless the metallic vapour has been projected from the electrode, there will be vapour in the space between the electrode and the point to which the material first vaporised has travelled, and it is possible that a pulse of luminosity is propagated through this, *i.e.*, that the particles are successively excited to luminescence without the vapour itself, as a whole, being in motion. A more complete discussion of this phenomenon is postponed to p. 343, but what here concerns us is that if this luminosity is propagated sufficiently rapidly it will reach the vapour produced at the commencement of the spark, which is still leading the way to the centre of the gap. Hence we should expect that when this occurs the streamer will suddenly bend over into line with the previous one and will then indicate the velocity with which the vapour originally produced is travelling. Then, after a further whole period, another streamer, excited by the third oscillation, begins at the electrode, and the same kind of procedure repeated, until when the streamer bends over into a line continuous with the second, the velocity of the vapour produced at the beginning of the spark is again indicated.

Thus we see that the velocity of the vapour in the electric spark is indicated by a kind of envelope consisting of the whole of the first streamer and of the latter portions of the following streamers until the middle of the gap is reached. What the photographs reproduced in this paper show to consist of an envelope was the line measured by SCHUSTER and HEMSALECH. SCHENCK* obtained such an envelope, but did not interpret it in this way.

If the metallic vapour remains luminous much longer than the time for which the oscillation which renders it luminous lasts, the streamers will not be separated in the moving photograph. This occurs apparently in the case of the calcium lines λλ 3969 (H), 3934 (K), 3737, 3706, when the spark is produced between poles of calcium metal. This causes the appearance of these lines in the moving photograph to be strikingly different from that of the lead and bismuth lines. Their edge is a sharp, bent line from which the intensity gradually shades off, the streamers being entirely obliterated. In the lead spectrum in which the calcium lines show strongly as an impurity, the streamers are separated and their structure is seen to be similar to that of the lead lines.

The magnesium line λ 4481 is shown in Plate 29, fig. 8, and the mercury lines λλ 4358, 4047, 3984, in Plate 29, fig. 9. The mercury was contained in a small cup and the upper electrode was, in this case, lead. The first streamer of the mercury lines is long, and in the cases of the lines λλ 4358 and 4047 the following streamers

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* SCHENCK, 'Astrophysical Journal,' 14, p. 116 (1901).

have a smaller inclination than the first. The streamers of the lead lines are seen to be shortened and the velocity is smaller.

In Table I. are given the average velocities in metres per second (V) of the various metals in the order of their atomic weights. The lines of type I. are those whose streamers form into an envelope, and type II. comprises the short lines which have a high velocity indicated by the first streamer only.

TABLE I.—Velocities.

Metal.	Lines.	Type of line.	V met./sec.	ρ (H = 1).	$V^2\rho/(64)^2$.
Magnesium . .	4481	I.	460	12	624
Aluminium . .	4530, 4521, 4479	II.	? 870	13·5	2,520
Calcium . . .	3969, 3934, 3737, 3706	I.	416	20	850
Zinc	4925, 4912	I.	388	33	1,200
Cadmium . . .	4416	I.	404	56	2,240
Tin	4586, 4216, 3908, 3861, 3745	II.	? 1370	60	27,400
Antimony . .	4693, 4592, 4352, 4265	II.	? 2230	60	80,000
Mercury . .	4358, 4047		936	100	21,500
	3984		1155		32,700
	4358, 4047 } from Cd amalgam (78 per cent. Hg)		532		
	3984		633		
Lead . . .	4387, 4245	I.	303	103	2,325
	4798, 4761, 3854	II.	1960		98,000
Bismuth . .	4302, 4260, 4079, 3864, 3793	I.	283	104	2,045
	4798, 4751, 4561, 3696, 3614	II.	2024		104,500

The effect of electric intensity on the velocity of the metallic vapour has been investigated by varying the capacity. A discharging key was introduced into the circuit and the spark made to pass by pressing the key when the Wimshurst had been rotated a certain number of times. In this way only the spark voltage was altered. The results are given in Table II. for different spark lengths. Whilst the variation of velocity is slight, the tendency is that the velocity increases with diminishing capacity, *i.e.*, with increasing voltage. SCHUSTER and HEMSALECH found the same tendency.

TABLE II.—Effect of Capacity on the Velocity.

Bismuth.

Length of gap.	Capacity = 0·0306 mfd.	= 0·0206 mfd.	= 0·0103 mfd.
centims.			
0·5	V = 295	= 340	—
0·8	283	316	= ? 457
1·2	317	? 496	332

The effect of self-induction has been found by lengthening and shortening the leads from the condensers to the spark electrodes. The results are given in Table III. In the first case the leads were as short as possible.

TABLE III.—Effect of Self-Induction on the Velocity.

Bismuth. Capacity = 0·03 mfds.

Length of gap.	Period = $2 \cdot 82 \times 10^{-6}$ sec.	$= 3 \cdot 88 \times 10^{-6}$ sec.	$= 4 \cdot 98 \times 10^{-6}$ sec.
centim. 0·8	V = 242	= 283	= 288

7. *Constitution of the Spark.*

(*a*) *Origin of the Velocity.*—We now proceed to discuss the problem of the constitution of the electric spark, and deal first with the propagation of the vapour into the spark gap. We have the following possibilities :—

(1) That the vapour diffuses towards the centre of the gap by the pressure suddenly developed at the electrodes.

(2) That the particles of vapour are charged and move under the action of the electrical field.

(3) That the particles are projected towards the centre.

The velocity of diffusion (or effusion) of the metallic vapour will be proportional to the molecular speed and independent of the amount of matter vaporised ; indeed, the velocity will, if there is no loss of energy in eddy currents, by cooling or by internal friction, and if the pressure developed is sufficiently great, be identical with the velocity of sound in the vapour, as has been verified in effusion experiments. This is given in metres per second by the relation

$$V = 64 \, (T/\rho)^{1/2},$$

where T is the absolute temperature of the vapour and ρ its density compared with that of hydrogen, if we neglect the ratio of the specific heats. Assuming that the temperature of the vapour is not very different in different sparks, we should expect that the velocity of the vapour would be inversely proportional to the square root of the density. In the last column of Table I. are given the values of T calculated from this equation on the assumption that the metallic vapours are monatomic. The high values for lines of type II. show that the velocity of the particles emitting these lines is due to some other cause than diffusion.

That the velocity is due to diffusion is certainly the simplest explanation of the phenomenon, and diffusion must, in any case, play a great part. It was not to be expected that the velocity of the vapour in the spark should be anything but approximately inversely proportional to the square root of the vapour density, for the disturbing influences may be considerable. Eddy currents of considerable magnitude apparently take place, as seen from the irregularities not only of the structure of the spectral lines but also of the "aureole" in the photograph of the spark itself. Since the vapour does not flow into vacuous space,* the velocity of the vapour will be retarded, though it is difficult to estimate the magnitude of this effect. The experiments on effusion show that the velocity does not fall appreciably until the back pressure approaches one-half that causing the effusion. However, if we increase this forward pressure by increasing the amount of matter vaporised, we shall reduce the effect of back pressure, and the velocity will probably, therefore, be dependent on the boiling-point of the metal. Attempts were made to find whether the amount of matter present had any effect on the velocity by introducing a small globule of mercury on one of the electrodes. The globule was small and probably disturbed the electric field, but it was seen that the velocity was 125 met./sec., compared with 936 met./sec. when a cup of mercury formed the electrode. The amount of matter vaporised is probably least for metals of high boiling-points, and the order of boiling-points is found to be approximately the reverse of that of velocities.

A second hypothesis is that the particles of vapour are charged. It is well known† that the resistance of the spark varies with the material of the electrodes between which the spark passes. We must, therefore, suppose that the metallic particles are participating in the carrying of the current, *i.e.*, that the vapour is ionised, or that the quantity of air which is ionised varies with the material of the electrodes. The period of the oscillations depends on the resistance of the circuit, and a change in the resistance should produce a corresponding change in the period. The periods for different electrodes are given in the following table; all lines in the same spectrum show the same period :—

Magnesium	$3\cdot70 \times 10^{-6}$ sec.	Antimony	$3\cdot76 \times 10^{-6}$ sec.
Aluminium	$3\cdot89$	Mercury	$3\cdot88$
Cadmium	$3\cdot74$	Lead	$3\cdot84$
Tin	$3\cdot73$	Bismuth	$3\cdot88$

It cannot, therefore, be said with certainty that the period varies with the material of the electrode.

Now, if the metallic vapour is ionised, then, as the direction of the electric field between the electrodes alternates, the vapour should be alternately impelled in one direction during one half of the period and in the opposite direction during the second half. There might be some lag of the reversal of the velocity behind the reversal of the field, for the kinetic energy already generated by the previous oscillation would

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* There will be a partial vacuum due to the sound-wave.

† FLEMING, "Principles of Electric-wave Telegraphy."

first have to be destroyed. No such change in the direction of motion of the vapour has been found in the streamers. In some cases, however, the envelope is not straight, but sinuous; where one streamer overtakes the previous one and falls into the envelope it indicates a higher velocity than the end of the previous streamer, and afterwards has a smaller velocity. This sinuosity is noticed in several photographs, but in the majority the envelope is straight. The acceleration and retardation of the vapour is coincident with the alternations in the field, but the retardation is not sufficient to reverse the direction of motion. The photographs show that the charge of the particles is negative. The successive alternations in velocity are 550, 130, 670, 190, 460 met./sec., the variation becoming smaller as the oscillations are dying out and as the vapour approaches the centre of the gap.

Unless discretion is used in selecting the point whose co-ordinates are measured, such variation in the velocity might be introduced where none exists. If a streamer does not actually run into the one following, there might be a tendency to take a reading on the steep part of the latter, which does not indicate the velocity of the vapour.

This sinuosity apparently would indicate that sometimes the metallic vapour is ionised. However, the action of the electrical field on charged particles cannot be the sole cause of the motion of the metallic vapour, for, owing to the reversal of the electrical field, the mean velocity during several periods would be small.

And, lastly, there is no evidence to support the hypothesis that the vapour is projected with the required velocity from the electrode.

It is, perhaps, fortunate that in any spectrum only two velocities are obtained. More than two would be difficult to explain. According to the simplest conception, viz., that we are dealing with a case of diffusion, the velocity would be inversely proportional to the square root of the vapour density, and it would seem simplest to suppose that the vapour which gives rise to the second class of line is more highly dissociated than that emitting the first class. If this is the case we must have, that if the vapour emitting the short lines of the bismuth spectrum is monatomic, that emitting the long lines contains five atoms to the molecule, which is very improbable. The impossible values obtained for the temperature of the vapour show that the velocity of the second class of line is not due to diffusion.

Another explanation might be that the short lines are emitted by charged molecules which are impelled with high velocity by the electric field, whilst the long lines are due to non-ionised vapour.

(*b*) *Propagation of Luminosity through the Vapour.*—Since we are most probably dealing with the diffusion of vapour from the electrodes, there will be vapour present in the space between the electrode and as far as the vapour starting at the first oscillation has reached. The electric current which is re-established in each oscillation can raise this vapour again to incandescence, and a streamer thus be produced. Where this streamer will start, whether at the electrode where there is always most vapour, or somewhere in the middle of the spark gap, does not appear at first sight from these considerations. The photographs show, however, that generally the vapour at the electrode becomes luminous first, but occasionally the luminosity is propagated also from a point within the gap both towards the centre of the gap and towards the electrode. The average velocity with which the luminosity is propagated through the vapour of bismuth has been found to be 800 met./sec. for λ 4260 and 2200 met./sec. for λ 4561. In the case of mercury the velocity of the vapour is larger than the velocity of propagation of luminosity through the vapour.

The luminosity which produces those portions of the streamers not forming part of the envelope is probably propagated in a manner similar to that of the luminosity of the air. In the moving photographs the air lines are not inclined sufficiently to be measurable. But this does not mean that the air molecules are moving with an exceedingly high velocity, and we should not expect a Doppler effect commensurate with such a velocity, for the air rendered luminous in the middle of the gap probably has not come from the electrodes. So in the atmosphere of metallic vapour in which streamers may be produced by the oscillations of the discharge we should expect to find streamers which are not due to a velocity of particles, and which will probably be steep.

8. *Duration of the Luminosity.*—The air lines are slightly broadened in the moving photographs. The amount of broadening shows that in $6 \cdot 9 \times 10^{-7}$ second the intensity has become insufficient to affect the photographic film. SCHUSTER and HEMSALECH found that the air line λ 3995 was thinner near the electrodes than in the centre of the spark. Now the air lines are generally fainter at the electrodes, and the apparent broadening of λ 3995 is seen to be due, at any rate in part, to two faint air lines near it, generally distinguishable in the moving photograph, but which at the electrodes are too faint to appear.

Stationary photographs measure the total amount of light falling on the plate whilst the spark is passing. Whether a line appears or not in the moving photograph depends not only on the intensity of the light, but also on the length of time for which the luminosity endures. Thus a line of short duration may be visible on the photograph when a line equally strong on the stationary, but of longer duration, may disappear. From their relative intensities in the moving photographs it is found that lines in the spark which also occur in the arc are of greater duration than the spark lines, and that the longer the line the greater is its duration, the short lines appearing also much sharper and finer than the long lines. It may be noted that SCHENCK, who measured the interval between the times when a line first appeared and when it last appeared, found this interval greater for the arc than for the spark lines.

9. *Summary of Conclusions.*

1. The velocity of the metal vapour is given by inclination of an envelope formed by the meeting of the first few streamers.

2. All lines of the same spectrum do not indicate the same velocity. They may be divided into two classes :—

(i.) Long lines, indicating the normal velocity ;
(ii.) Short lines, indicating a greater velocity.

3. The velocity is greatest near the electrodes, and falls away to a nearly uniform velocity.

4. The velocity of lines of type I. is probably due to diffusion ; that of type II. and of the mercury lines is too large to be explained in this way.

5. The envelope indicating the velocity of the vapour is occasionally sinuous, indicating that the particles are in these cases charged.

6. The velocity varies little with the spark voltage or with the self-induction of the circuit.

7. The velocity is apparently dependent on the amount of matter vaporised, and is, generally speaking, less for a metal of higher boiling-point.

8. The luminosities of the streamers of the short or "spark" lines are of shorter duration than those of the long or "arc" lines.

9. The streamers start at both electrodes, but are stronger when the electrode is negative, except the first streamer from the initially positive electrode. The streamers from the positive electrode are but rarely seen in the lines of longer duration.*

10. The period of the circuit is practically independent of the material of the electrodes.

My best thanks are due to Professor SCHUSTER for his interest throughout the research and for many valuable suggestions ; also to Professor RUTHERFORD and the staff of the laboratory for numerous suggestions. I have been indebted to Mr. C. RILEY, B.Sc., for his careful assistance in making the experiments and measuring the photographs.

[*April 3.—In the paper as originally presented this sentence ran as follows :—"The streamers from the positive electrode are only seen in the lines of short duration."]

ADDENDUM.

[*Note added April* 3.—The drawing reproduced on p. 338 *supra* has been prepared at the suggestion of one of the referees, and shows, with all the clearness of the original negative, the first edge of each streamer of λ 4387 in fig. 5 (Plate 29), which contains few accidental irregularities.

The referee suggests that the positive streamers are curved and the negative ones straight, this explanation bringing the phenomena of the spark more into line with those of the arc.

The presence of positive streamers in the long lines is exceptional, but in all cases the edge of what I have considered as one negative streamer forms a perfectly continuous line throughout its length. In several photographs instances occur where the positive streamer runs side by side with the negative (*e.g.*, in λ 4387 of fig. 5, the 5th + and 6th − at the upper electrode), the bend in the negative streamer taking place before the positive has met it.

If we are dealing with one of the negative streamers which fuse together into an envelope, *i.e.*, in which the streamer has again raised to incandescence the vapour produced at the commencement of the spark, the streamer ceases to be a pulse of luminosity on overtaking this vapour which is leading the way to the middle of the spark gap and must become inclined, since the vapour is travelling slower than the pulse of luminosity. It therefore seems to me to be not the simplest explanation to ascribe this inclination to a positive streamer previously almost invisible.

In those later pulses of luminosity which do not overtake the diffusing vapour it would be difficult to explain why the pulse from the negative should stop dead in the middle of the vapour at a distance shorter than that to which previous pulses have extended, and how the positive pulse, previously faint or invisible, should at this instant burst into intense luminescence.

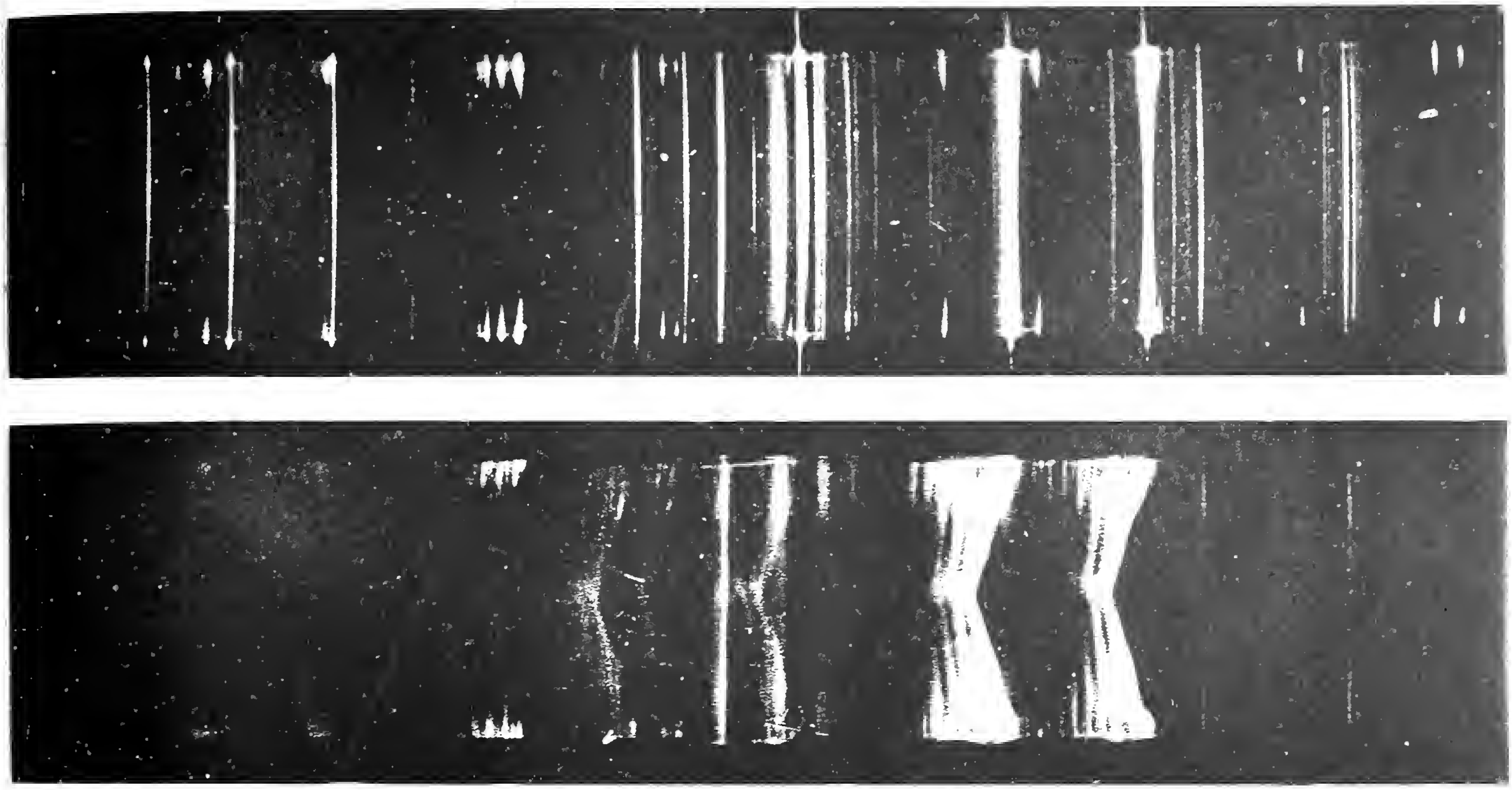
As regards the sinuosity of the envelope, the points of discontinuity are where the streamer meets the negative streamer and not the positive, as the referee's suggestion requires, *e.g.*, at the points in the drawing marked A and B, but not at C. My present opinion is that the cause of the sinuosity is the alternation in the temperature of the metallic vapour.

The crossing point of the two envelopes in fig. 5 is very slightly nearer the upper electrode (2 millims. in an enlargement in which the width of the spectrum is 68 millims.), but this is by no means a rule; in general the inclination of the envelopes is the same at the two electrodes.

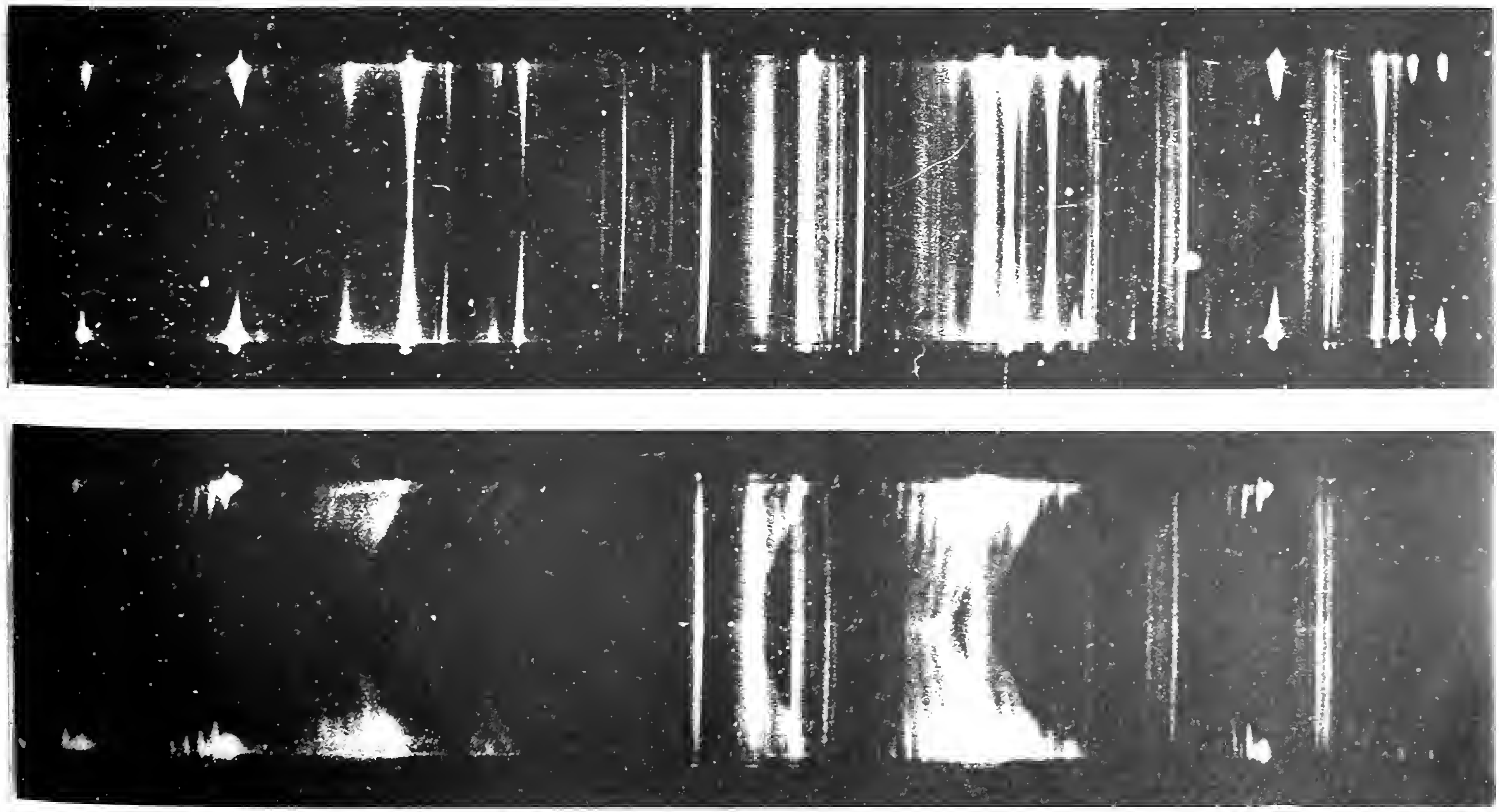
Photographs have already been taken with larger self-induction, but they do not give any information on the point, for the streamers die out before the following ones overtake them.

It is to be observed that the spark described by HEMSALECH in 'Comptes Rendus,' 142, 1511 (1906), was produced under very different conditions from mine, and that in it the negative luminosity did not travel into the spark gap. WALTER, in 'Ann. d. Phys.,' 21, 223 (1906), and SCHENCK, in 'Astrophys. Jour.,' 14, 116 (1901), find that the streamers come from the negative electrode, and the former seeks to explain it as due to kathode disintegration.

It would be an important acquisition to our knowledge if our views of the phenomena in the electric arc could be found to apply also to the spark, but I do not think that the photographs support the suggestion.]



Figs 1 and [illegible]



Figs 3 and 4 — Bismuth.

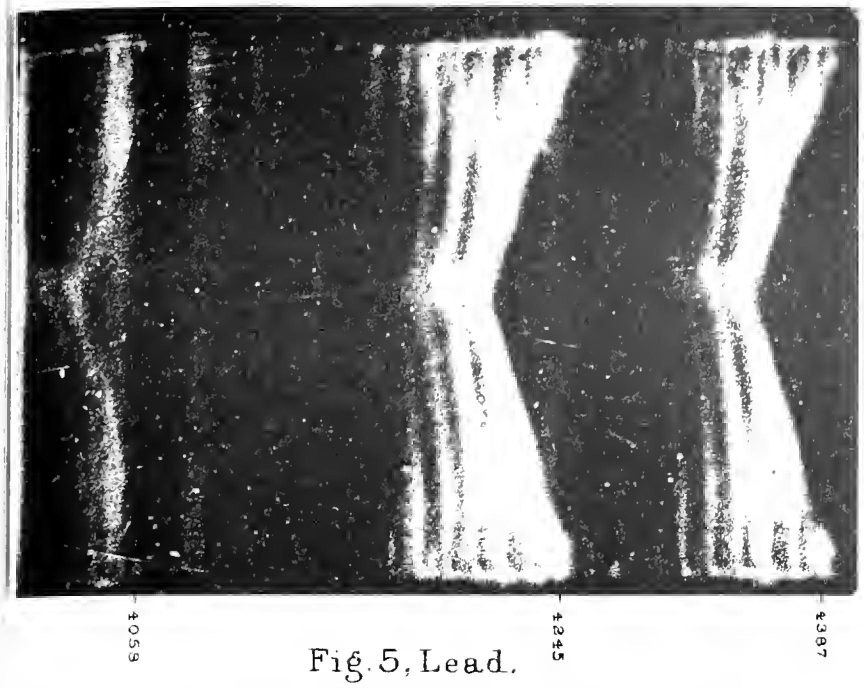


Fig. 5, Lead.

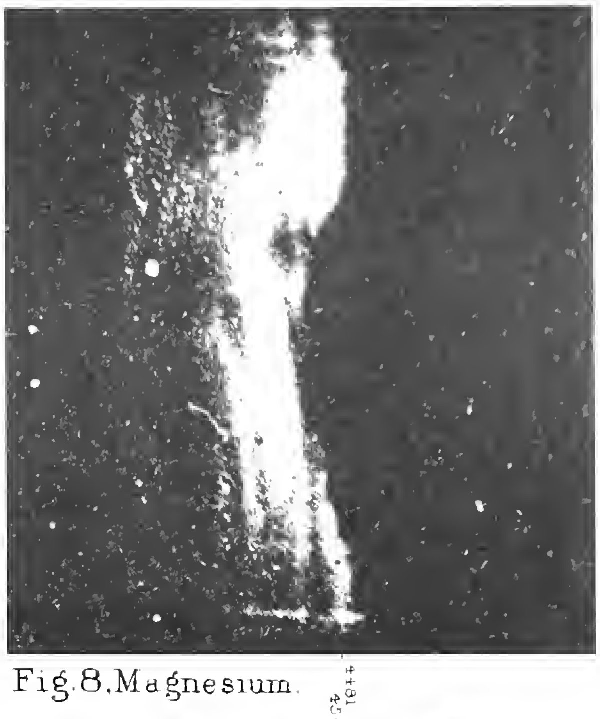


Fig. 8, Magnesium.

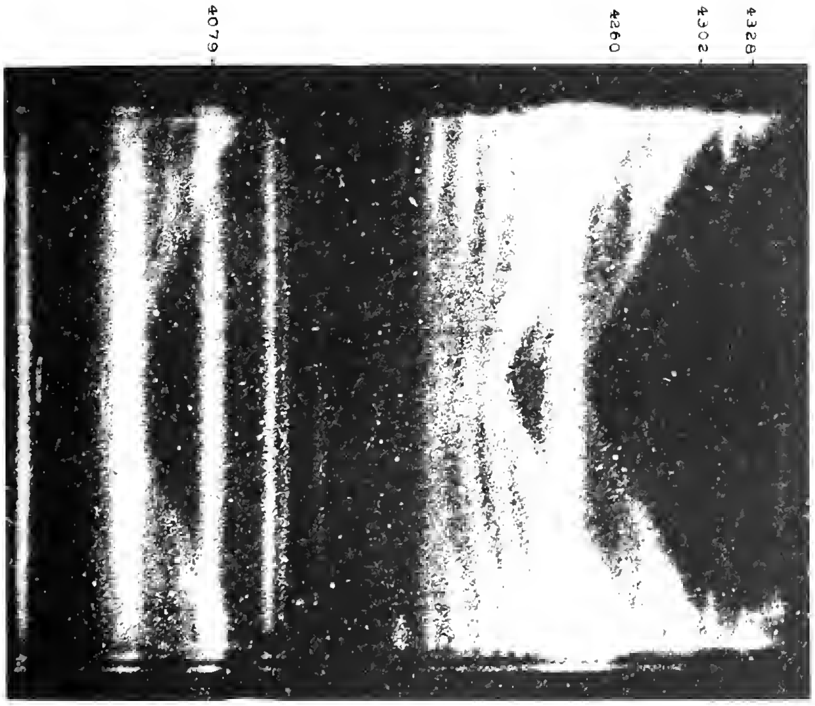


Fig. 6, Bismuth.

Fig. 7. Bismuth

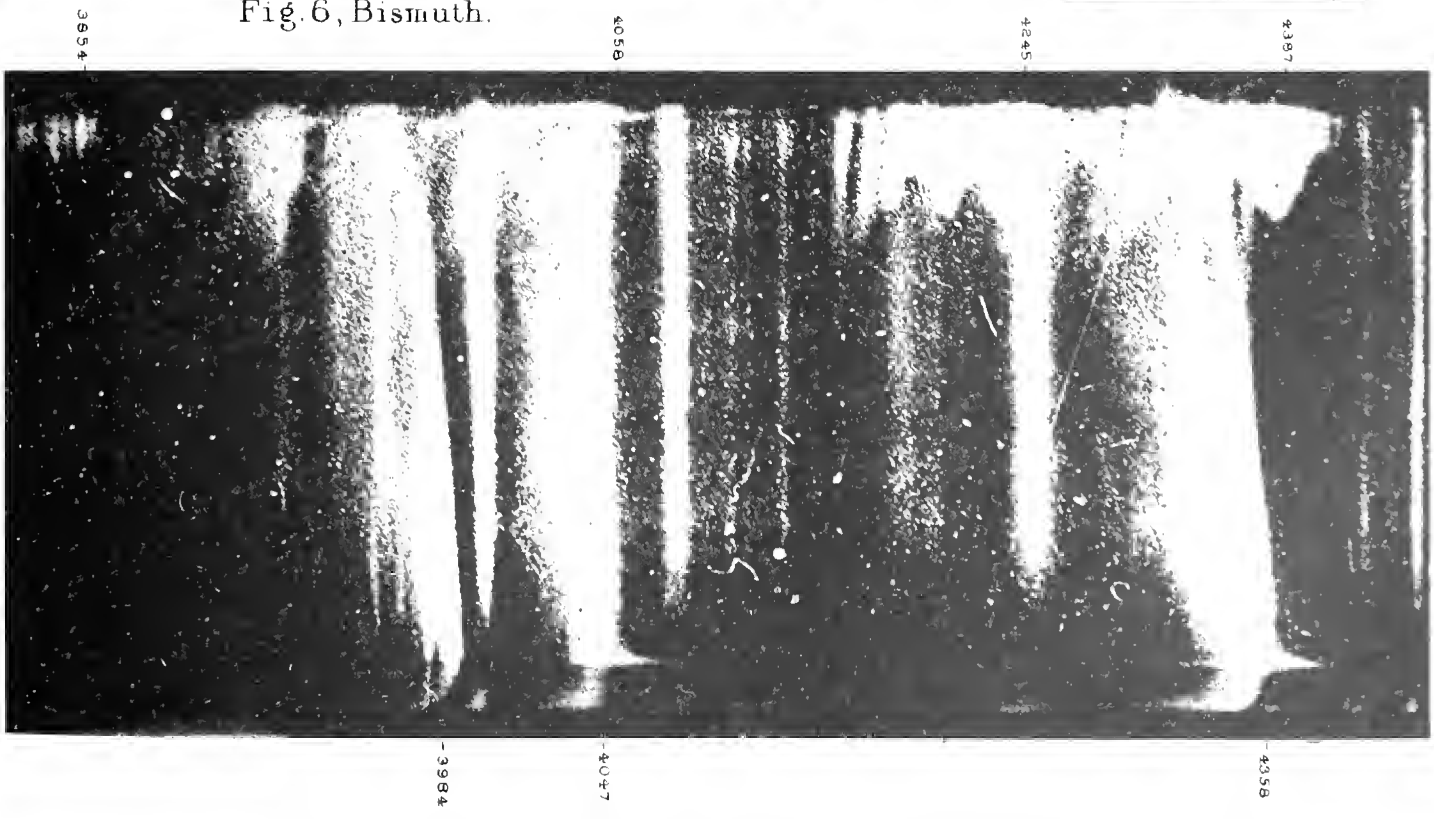


Fig. 9, Upper electrode Lead, lower electrode Mercury.

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THERMAL RADIATION IN ABSOLUTE MEASURE AT VERY LOW TEMPERATURES

BY

J. T. BOTTOMLEY, M.A., LL.D., D.Sc., F.R.S.,

AND

F. A. KING.

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X. *Thermal Radiation in Absolute Measure at Very Low Temperatures.*

By J. T. BOTTOMLEY, *M.A., LL.D., D.Sc., F.R.S., and* F. A. KING.

Received June 15,—Read June 27, 1907.

CONTENTS.

INTRODUCTION.

1. THE experiments described in the following paper form part of an investigation with which one of the present authors has been engaged for many years past. The object of this investigation is the direct determination, in absolute measure, of the loss of energy, from a heated body to cooler surroundings, under differing conditions as to (1) the dimensions of the cooling body; (2) the nature of the surfaces of the cooling body and of the enclosure; (3) the mean absolute temperature of the cooling body and the envelope; (4) the nature of the atmosphere surrounding the cooling body. Several papers have already been published on this subject in the 'Philosophical Transactions of the Royal Society' and in the 'Proceedings,' and have been communicated to the British Association and elsewhere.* In all of these the lowest temperature available was the atmospheric temperature, or rather the temperature of the water supply of the laboratory; and the body from which radiation was to take place was heated to a temperature as much above the atmospheric temperature as the circumstances connected with the experiment would, from time to time, permit. Thus the upper and lower limits of these experiments have been something below 1000° C. as the highest temperature of the cooling body, and, say, 10° C. as the lowest temperature of the enclosure.

2. Some time ago, through the kindness of Lord BLYTHSWOOD, F.R.S., an unlimited supply of liquid air was placed at our disposal, to be followed later by a supply of liquid hydrogen. It seemed therefore most desirable to extend the research in the

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* 'Phil. Trans.,' 1887 and 1893; 'Brit. Assoc.,' 1884, 1901, 1905, &c.

direction indicated by the new facilities given to us, which both greatly extended the limits governing the enquiry, and also made it possible to obtain determinations, in absolute measure, of thermal radiation between bodies at extremely low temperatures. It seemed specially interesting, for example, to determine, in absolute measure, the radiation under given circumstances from a body at, say, ordinary atmospheric temperature, to an enclosure at a temperature which may perhaps approximate to that of space. With the exception of some preliminary results, which were communicated 18 months ago to the British Association, nothing of the kind has been published, so far as we are aware.

3. The main object of the present paper is to give an account of this research. We have also, however, made an endeavour to sum up, and bring into co-relation, the results of earlier experiments, made under various circumstances, with forms of apparatus differing widely from each other, with different radiating surfaces and different enclosures, or sometimes with the same apparatus after it has been dismantled and re-erected. Finally, we have made an attempt to apply the law of STEFAN to the results, in order to obtain some idea as to how far the conditions under which it holds have been realised in these experiments.

DESCRIPTION OF THE APPARATUS EMPLOYED.

4. Although the apparatus used has already been described in former papers, a short description of it here will probably be of advantage, particularly as it was

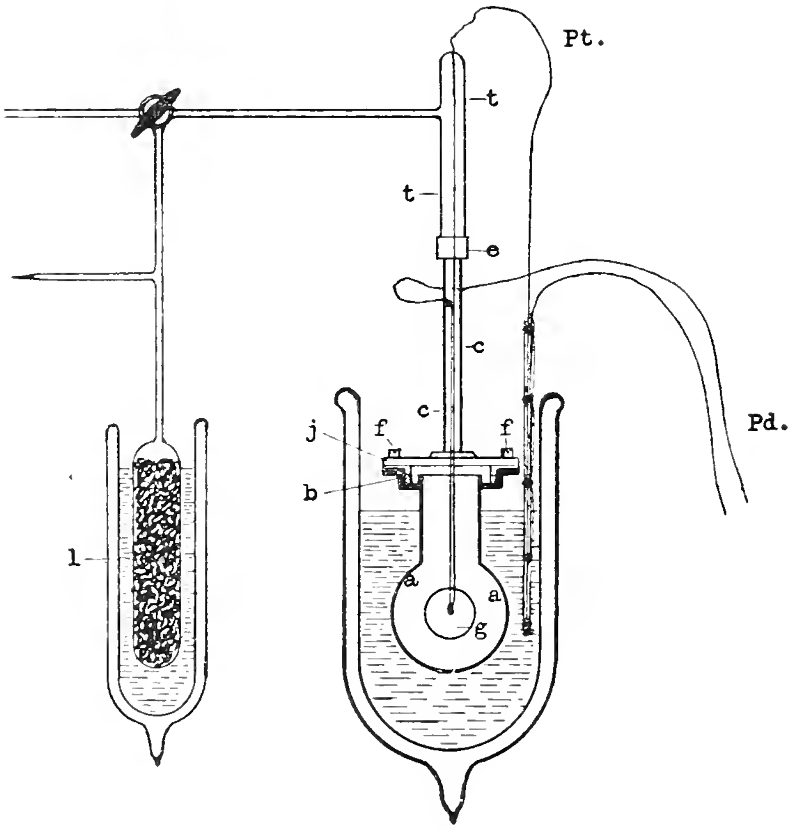

Fig. 1.

necessary to alter the arrangements considerably, in order to make them suitable for low-temperature work.

5. The bodies used in these experiments for radiation purposes are solid copper globes, 4 centims. in diameter. These globes, and the enclosure in which they are suspended, were used in many earlier experiments on radiation at high temperatures; and the main parts of the apparatus used then and of the present apparatus are essentially the same. As has been already mentioned, however, modifications had to be introduced, owing to the low temperature to which the enclosure was subjected.

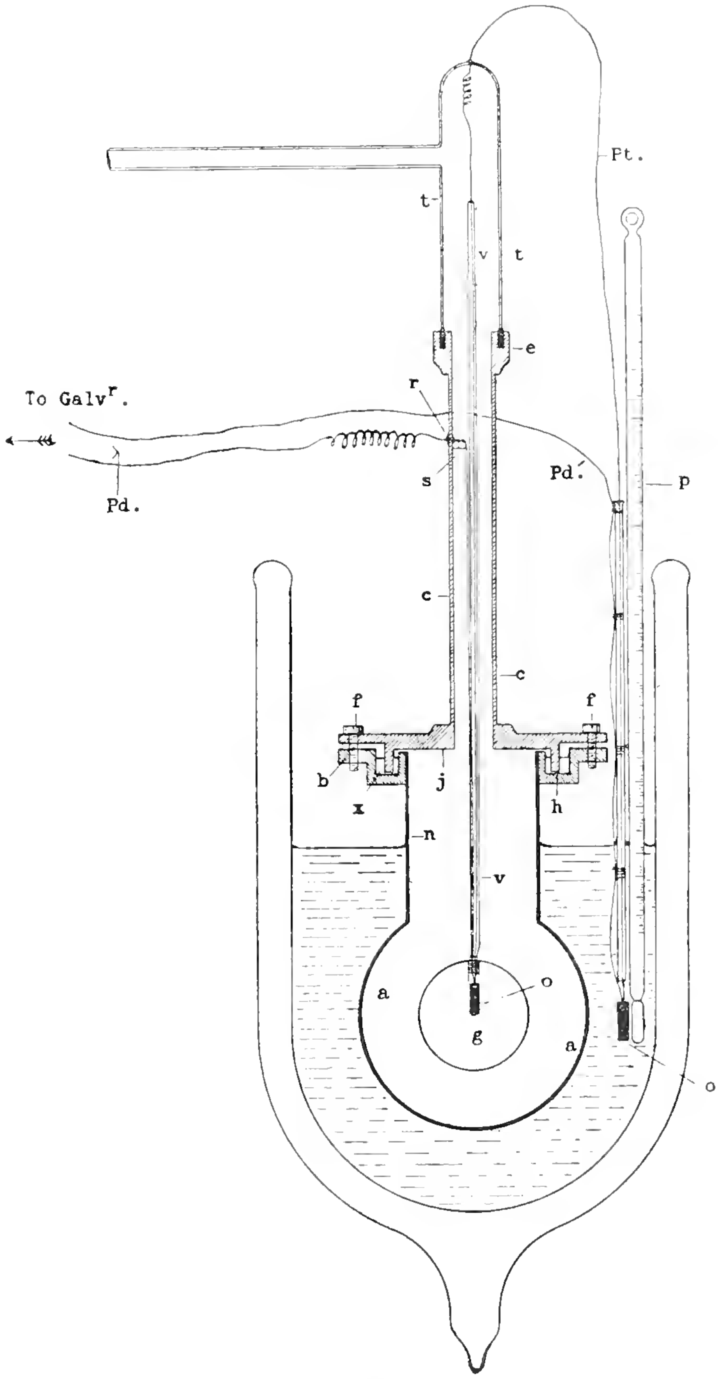

Fig. 2.

6. Referring to the general sketch of the apparatus, fig. 1, and to fig. 2: at the centre of a spherical copper shell *aa*, 8 centims. in diameter, a copper globe *g* is suspended. The

enclosure was beaten into shape out of a piece of thick sheet copper. It has a brass, cup-shaped flange, *b*, brazed on to the neck *n*, and the whole is thoroughly tinned both inside and outside, to make sure that every crack or pin-hole shall be filled in and the enclosure made vacuum tight. A seamless brass tube, *cc*, about $1\frac{1}{4}$ centims. in internal diameter, has the corresponding flange, *j*, brazed on to its lower end, and has a collar, *e*, with a U-groove turned in it, soldered to its upper end. When the enclosure is brought up into position, the shoulder of the upper flange, *j*, fits into the cup of the flange on the enclosure, and the two are firmly clamped together by the four set-screws *ff*. The joint is then made vacuum-tight by pouring molten fusible metal into the cup, *x*, the flanges having been previously prepared by tinning them with fusible metal.* Fusible metal was used on account of its low melting-point, as the prolonged heating necessary to make a good soldered joint of such extent has a tendency to tarnish the highly polished silvered globe when it is suspended within the enclosure. A piece of wide glass tubing, *tt*, was ground to fit the groove in the collar *e*; and, when all other preparations were complete, the joint was carefully sealed with "Siegelwachs." To prevent the "Siegelwachs" from becoming brittle by the cold conducted up the brass tube *cc*, when the enclosure is immersed in a bath of liquid air, copper vanes were clamped to the upper part of the brass tube to act as a radiator. A T-piece of quill tubing was sealed on to the glass tube *t*, to connect the enclosure to a pair of five-fall Sprengel pumps which are arranged to run continuously. Interposed between the pumps and the enclosure is a M'Leod gauge† for measuring the vacuum pressure; and attached to a three-way stopcock there is a bulb, *l*, filled with cocoanut charcoal, which can be put in communication with the enclosure.

7. All the joints between the various pieces of glass apparatus are fused together with the blow-pipe, so as to avoid rubber, or other such connections.

Thermojunctions.

8. For measuring the difference of temperatures between the globe and the enclosure, a pair of platinum to platinoid thermojunctions are used. These two metals give an excellent thermo-electric combination, as was shown in a paper on the subject by J. T. BOTTOMLEY and A. TANAKADATE.‡ We have found them very satisfactory.

The two thermojunctions are soldered into two little copper cylinders, *oo*, about

---

* While working with fusible metal we have found that this material becomes springy at liquid-air temperature, and thus yields elastically to any changes in shape of the flanges.

† An improvement was made in the present apparatus by placing the M'Leod gauge as close as possible to the enclosure of which the vacuum pressure is to be measured by the gauge. We have found, from past experience, that it takes a considerable time for small differences of pressure to become equalised in highly exhausted enclosures, especially when the rarefied gases have to diffuse through a length of glass tubing.

‡ 'Roy. Soc. Proc.,' vol. 46, 1889, p. 286.

1 centim. long and 0·4 centim. in diameter. One of these cylinders is screwed into the centre of the copper globe, and the other, carrying the outside thermojunction, is tied to the bulb of a pentane thermometer *p*, and is placed in the bath of liquid air which surrounds the enclosure.*

9. The cooling globe *g* is suspended by the wires of the thermojunction. Its weight is borne by the platinoid wire, which passes through a fine hole drilled in the wall of the brass tube, and the wire is guided to hang centrally in the tube by the support *s*. After the length of the platinoid wire has been adjusted so that the copper globe shall hang at the centre of the spherical enclosure, the wire is soldered at the point *r*, where it passes through the wall of the tube. The platinum wire passes out through a sealed joint in the roof of the glass tube *tt*, and to insulate it from the platinoid wire, and from the brass tube in which the two hang side by side, the platinum wire is enclosed in a fine glass tube or sleeve, *v*, which completely protects it.

10. The ends of the thermojunction circuit are brought to a mercury reversing key, which has four cups. To the copper electrodes of one pair of cups the thermojunction wires are soldered; and the electrodes of the other pair of cups are joined up, through an Ayrton Universal shunt, and a 100,000 ohms resistance, to a standard Clark cell. Two amalgamated copper rods, the terminals of the galvanometer circuit, can be revolved so as to make contact with either pair of mercury cups. This allows the constant of the galvanometer, and the thermojunction value, to be checked with reference to the value of the standard Clark cell whilst the experiment is proceeding. No joints exist between the thermojunctions and the cups of the mercury key, the platinoid wires of the thermojunctions being taken direct to the mercury cups; and wherever there are joints in this circuit they occur in pairs, and the corresponding joints are insulated and placed side by side, and then wrapped in a thick protective covering of cotton wool. All connections exposed to draughts, or likely to give rise to thermo-electric currents, were covered up with cotton wool.

Galvanometer.

11. Owing to the passing of electric trams in the vicinity of the Laboratory, we were obliged to abandon the dead-beat Thomson reflecting galvanometer of the old pattern (having a small mirror backed with four tiny magnets, hung by means of a spider line, at the centre of the galvanometer coil), which was used on former occasions and found thoroughly satisfactory. A Kelvin marine type of moving-coil galvanometer was substituted for it, and was made extremely sensitive and dead-beat; and was also adjusted to give proportional deflections. This, used with a Steinheil telescope, placed 1 metre distant from the galvanometer mirror, and with

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* To prevent the thermojunction wires from touching one another in the liquid air bath, the platinum wire is enclosed in a piece of thermometer tubing, and the platinoid wire is tied at intervals to the outside of the tube. This allows the junction to be moved about in the bath without fear of disturbing the wires.

a circular scale 1 metre in radius ruled in half millimetre divisions, gave results which left nothing to be desired. The telescope, galvanometer, and each part of the radiation apparatus, were fastened firmly down, to prevent any alteration taking place after the thermojunctions had been calibrated.

Calibration of the Thermojunctions.

12. To calibrate the thermojunctions for low temperatures was not a simple matter. The difficulty was to get a number of reliable points between the temperatures 0° C. and $-200°$ C. The method ultimately adopted is similar to that used, in J. T. Bottomley's earlier experiments on radiation, for determining the resistance of a platinum wire at high temperatures; but it was suitably modified for the present requirements, and for dealing with low temperatures.

13. A thick double-walled copper tube was taken, and one end immersed in a Dewar flask filled with liquid air, fig. 3. The end *a* projecting out of the flask was at atmospheric temperature, say 16° C.; and the portion immersed, *b*, at $-194°$ C., the boiling point of liquid air. Between the points *a* and *b*, along the length of the tube above the surface of the liquid air, there was a fairly uniform temperature gradient, which was maintained with the greatest steadiness.

One of the little copper cylinders *o*, into which the thermojunctions are soldered, was tied to the bulb of a pentane thermometer *p*, reading from $+30°$ C. to $-200°$ C. This thermometer had previously been compared with a standardised Reichsanstalt pentane thermometer, and checked by a hydrogen thermometer, and by a platinum resistance thermometer. The other thermojunction was within the copper globe, and inside the enclosure, as shown in the diagram. In taking observations, the junction in the copper globe was kept at a known fixed temperature by surrounding the copper enclosure with ice, or water at the temperature of the laboratory, or with liquid air. The pentane thermometer with the junction attached was lowered into the copper tube, and, by placing it at different heights, series of temperatures were obtained which remained absolutely steady whilst the galvanometer readings were being taken. By raising or lowering the flask of liquid air, or by adjusting the height of the copper tube above the surface of the liquid air, or by raising or lowering the little copper cylinder from point to point in the copper tube, it was easy to find any required point of temperature throughout the whole range of the pentane thermometer. When the readings of the pentane thermometer and galvanometer showed that the thermojunction in the copper tube was at a steady temperature, a stop-watch was started; and if at the end of two minutes no alteration had taken place in the thermometer and galvanometer readings, the galvanometer deflections to the right and left of zero were observed, and then the zero was taken.*

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* This method of obtaining a series of known fixed temperatures, high or low, is most convenient; and is far superior to any other with which we are acquainted.

14. The results obtained were plotted as a curve, taking the sum of the galvanometer readings as ordinates, and the difference of temperatures between the thermojunctions as abscissæ. From this curve the temperatures corresponding to the observed galvanometer deflections were read off when it was required to convert thermojunction readings to temperatures on the Centigrade scale.

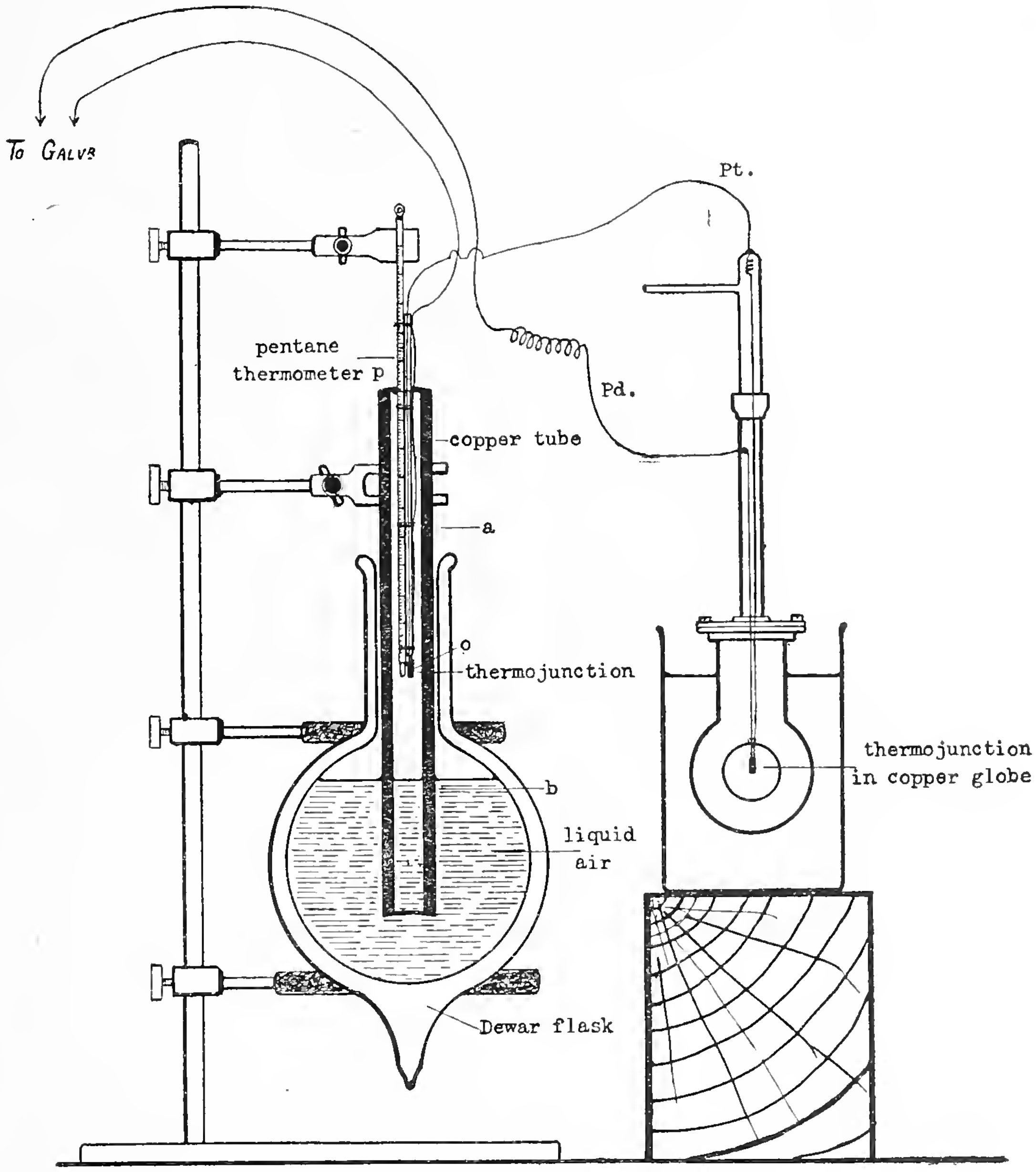

Fig. 3. Calibration of thermojunctions.

This curve was plotted on a large scale on a table covered with a sheet of plate glass, 4 feet 6 inches by 3 feet 6 inches, ruled in 10-centimetre squares. The glass plate was not wholly covered with squared paper; those squares only through which the curve passed were filled in. The smallest division of the squared paper is equal to 1 mm., and this corresponds to 0·1° C., or one scale division of the galvanometer.

15. The results of confirmatory experiments, made after intervals of months, agreed with absolute accuracy; which showed that both the thermojunctions and the galvanometer were quite constant.

METHOD OF CONDUCTING AN EXPERIMENT.

16. Before commencing an experiment, the apparatus, and the tubes connecting it to the Sprengel pumps, are thoroughly dried out. The sooted or silvered globe, as the case may be, is then attached to the copper plug *o*, into which the thermojunction is soldered. When an experiment is being made with the sooted globe, the globe receives a fine dead-black coating of soot from a small gas jet when it is hanging in position on the thermojunction wires. The enclosure *aa* is also given a coating of soot on the inside, and is then brought up into place and clamped to the upper flange by the set screws *ff*, which pass through holes drilled in lugs cast on the flanges. The joint *h* between the flanges is next made tight by pouring molten fusible metal into the cup *x* till the joint is well covered. A small blowpipe jet is run over the surface of the fusible metal just after it has set, to make sure that no pin-holes are left in the joint.

The preliminary exhaustion of the apparatus is made with a two-cylinder Fleuss mechanical pump, which very rapidly produces almost a barometric vacuum. Then the Sprengel pumps are set working, and they continue to run until a high vacuum is obtained. When, after repeated heating, the last traces of moisture and the occluded gases have been driven from the enclosure and charcoal bulb, the pumps are shut off temporarily, and the M'Leod gauge and charcoal bulb, *l*, are left in communication with the enclosure. The charcoal bulb is then immersed in a vessel of liquid air, which causes the collapsible gases to be absorbed by the charcoal and condensed, or frozen. This greatly improves the vacuum, and it clears the enclosure of traces of mercury vapour which may have diffused through from the pumps, a matter of the highest importance.

17. The next operation is to check the galvanometer with the standard Clark cells, in order to ascertain that its constant has not altered since the calibration of the thermojunctions. When this has been done, liquid air is poured into the Dewar vessel surrounding the enclosure, and as soon as the violent ebullition has subsided, denoting that the enclosure has cooled down to the temperature of the liquid air, observations commence.

18. Readings are taken every 2 minutes at the beginning of the experiment, and later on at intervals of 5 minutes, the frequency depending on the state of the vacuum, and the rate of cooling of the globe.

A chronometer, beating half-seconds, is placed close to the observer at the reading telescope. At 15 seconds before the exact minute the mercury switch is closed and the deflection to the right of zero observed. The switch is instantly reversed, and at 15 seconds after the minute the galvanometer has come to rest and the deflection to the left of zero can be read. The switch is then opened and the zero of the galvanometer is taken. The vacuum pressure, and the temperature of the liquid air, are read at intervals and noted alongside the readings with which they correspond. Also, the observations, as they are made, are plotted on squared paper. The cooling curves thus obtained afford a good check as to the working of the thermojunctions, while they keep the observer informed as to the steadiness of the cooling process.

19. To allow for evaporation of the liquid air, and to keep the level in the Dewar vessel up to a fixed mark on the enclosure, a small quantity of liquid air is added every 5 minutes. The temperature of the enclosure is kept constant by this method. It was found that adding fresh liquid air in large quantities caused irregularities on the cooling curves, which were observable as the readings were plotted.

20. Trouble was sometimes caused by the leaking of the copper shell, which, owing to the extreme temperature to which it was cooled, would get strained, and allow a slight leakage to take place at the joints or the brazed seams. These leakages disappeared when the liquid air was removed. They were, however, often overcome, and the vacuum kept up to a constant pressure by the Sprengel pumps and the charcoal bulb. Latterly the leakage was got rid of by keeping a layer of pentane over the fusible metal covering the joint between the flanges, and by painting the outside of the enclosure with collodion varnish.

Calculation of Results.

21. We will now explain the method of calculating the results. For this purpose we use an equation of the form

$$-c\frac{dv}{dt} = e\mathrm{S}\,(v-\mathrm{V}),$$

where v is the temperature of the cooling globe, V that of the enclosure, c the capacity for heat of the globe, and S its surface, while e is a coefficient which has been called the *Emissivity*. It is easy to show by an application of FOURIER'S equations that, to a first approximation sufficient for our present purpose, the loss of heat by conduction by the thermojunction wires may be allowed for by adding to S, or rather eS, a small quantity depending on the diameter, conductivity, and emissivity of the wires, the length of the wires being so great that no heat passes away by conduction at the ends.

22. A point requiring consideration is the following :—The arrangements explained above give approximately the temperature at or near the centres of the copper globes. In a criticism of D. MACFARLANE'S experiments, which were carried out in 1872 with the same globes which we have used and under circumstances precisely similar, M. CORNU, 'Journal de Physique,' December, 1873, raised an objection to the thermoelectric method as compared to the method used by DULONG and PETIT, where the bulb of a thermometer was a cooling body, on the ground that the temperature at the

centre may be different from that of the surface.[*] This objection was completely answered by numerical calculations founded on the dimensions and conductivities of the globes in question; and, in an interesting appendix, the whole question is discussed in 'Roy. Soc. Proc.,' June 10, 1875.[†]

23. In the above formula the coefficient e corresponds to the *emissivity*; it is the quantity of heat lost per second, per square centimetre of surface, per degree centigrade of difference of temperatures of radiating surface and surroundings. This formula is commonly taken to be a representation of the "law of cooling," whether in air or in any other gas, or in vacuum, the range of temperature dealt with being moderate. The numerical value of e depends on the circumstances under which the cooling takes place, and, when air is present, on the dimensions and shape of the cooling body.

24. One way of dealing with the matter, from an experimental point of view, is to solve the equation above as though e were constant—which is, of course, approximately true if the difference of temperatures is small—and then to determine numerically the value of e at different places in the temperature scale, taking an exact account of the circumstances. When a sufficiently large number of such values have been obtained, a basis for a wider theory will have been laid.

Taking, then, the equation

$$-c\frac{dv}{dt} = eS(v-V),$$

and its solution

$$\log_\epsilon \frac{v_0-V}{v-V} = \frac{eS}{c}t,$$

where v_0 is the temperature of the cooling globe when $t = 0$, and V the temperature of the enclosure, we have for the numerical calculation of e, using common logarithms, M being their modulus,

$$e = \frac{Mc}{St_1}\{\log(v_0-V) - \log(v-V)\}.$$

Here $t_1 = 300$, the interval of time used in our experiments being 5 minutes; $c = 25{\cdot}482$, and $S = 50{\cdot}26$, to which we must add a small quantity which we roughly estimate at about 0·6 per cent.—the correction applied for the carrying away of heat by the thermojunction wires. This we calculate, assuming that the emissivity of the surface of the conducting wires is much the same as that of a tolerably clean silvered surface.

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[*] To find experimentally how long it would take for a wave of heat to travel from the surface to the centre of the copper globe, a spirit flame was applied to the outside of the globe, and the instant of application was taken with a stop-watch. The flame was kept under the globe for 2 seconds, and in 6 seconds the zero of the galvanometer scale was seen to be moving rapidly across the field of the observing telescope. The maximum deflection was obtained in less than 20 seconds from the time of applying the spirit flame.

[†] Republished in Lord KELVIN'S 'Collected Papers,' vol. 3, p. 245.

25. The emissivities in the present paper are calculated by two methods. To explain the working out of the results we cannot do better than quote two specimen pages out of the calculation note-books. These pages are not selected because they show any special feature; they are simply average specimens.

Method 1.

26. This method of calculating the emissivities is the one chiefly used in the former paper, 'Phil. Trans.,' 1893. It is fully explained and illustrated there in an appendix, and a brief description of it here will suffice. Referring to p. 360: Column 1 contains the times, against which the corresponding galvanometer deflections are noted in Column 2. These deflections correspond to the differences of temperatures between the thermojunctions,[*] and give the temperatures of the globe at those particular instants of time. Taking the common logarithms of Column 2, we get Column 3; and the difference between the successive logarithms of the deflections give us Column 4. To obtain the emissivities from the numbers in Column 4, they must be multiplied by $(\mathrm{M} \times c) / (300 \times \mathrm{S})$, the value of which is $3{\cdot}868 \times 10^{-3}$. This constant is smaller than that used in the 1893 paper on account of a reduction in the numerical value of c which it has been necessary to make for the diminished value of the heat capacity of the copper globes, owing to the low temperatures of the experiments.[†]

27. The differences of the temperatures of the globe and its surroundings are read off from the thermojunction calibration curve already mentioned, § 14, and these are placed in Column 6; and Column 7 contains the arithmetic means of the successive pairs of these numbers.

By adding the absolute temperature of the surrounding bath to the latter temperatures we get the absolute temperatures of the globe. These are placed in Column 8.

Method 2.

28. In the second method the series of observations during any one experiment, lasting perhaps $2\frac{1}{2}$ hours or more, are taken as a whole; and the emissivities at various temperatures, from the highest to the lowest, are calculated as a continuous series; the emissivity being supposed to alter continuously with the absolute temperature of the cooling body.

For purposes of numerical calculation, however, the observed deflections, and the logarithms of these numbers, are, in this method, expressed as functions of the time reckoned from the beginning of the experiment in the way which is about to be

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[*] In Dr. BOTTOMLEY'S 1893 experiments it was necessary to apply certain corrections to the galvanometer readings: (1) for the straight galvanometer scale used; and (2) a thermojunction correction. These were described among the details of calculation. They are not required here owing to our present improved arrangements.

[†] U. BEHN, 'WIEDEMANN'S Annalen,' 66, 2, pp. 237–244 (1898); 'Annalen der Physik,' 1, 2, pp. 257–269 (1900). SCHMITZ, 'Proc. Roy. Soc.,' 72, pp. 177–193 (1903).

April 2, 1906.

SILVERED Globe Cooling in Vacuum.

Vacuum = 0·06 **M**. Temperature of Enclosure = 79° abs.

	1.	2.	3.	4.	5.	6.	7.	8.
Number.	Time.	Galvanometer deflection.	Logarithm of deflection.	Differences of logarithms.	Emissivity.	Difference of temperatures of globe and enclosure.	Mean difference of temperatures of globe and enclosure.	Absolute temperature of globe.
	A.M.					$t-t'$ ° C.	° C.	
1	10.20	867·1	2·938069			212·0		
				·003066	5·930 × 10^{-6}		210·15	289°·15
2	30	861·0	·935003			208·3		
				·002986	5·773 ,,		206·55	285·55
3	40	855·9	·932017			204·8		
				·002905	5·618 ,,		203·10	282·1
4	50	849·4	·929112			201·4		
				·003027	5·853 ,,		199·75	278·7
5	11.00	843·5	·926085			198·1		
				·002996	5·793 ,,		196·50	275·5
6	10	837·7	·923089			194·9		
				·002966	5·735 ,,		193·35	272·3
7	20	832·0	·920123			191·8		
				·002985	5·771 ,,		190·35	269·3
8	30	826·3	·917138			188·9		
				·002848	5·507 ,,		187·55	266·5
9	40	820·9	·914290			186·2		
				·002919	5·452 ,,		184·85	263·8
10	50	815·4	·911371			183·5		
				·002833	5·478 ,,		182·25	261·2
11	12.00	810·1	·908538			181·0		

12	10	804·9	·905742	·002796	5·532 „	178·7	179·85	258·8
13	20	799·7	·902927	·002815	5·431 „	176·5	177·60	256·6
14	30	794·7	·900203	·002724	5·268 „	174·4	175·45	254·4
15	40	789·8	·897517	·002686	5·194 „	172·4	173·40	252·4
16	50	785·1	·894925	·002592	5·012 „	170·5	171·45	250·4
17	1.00	780·4	·892317	·002608	5·043 „	168·8	169·65	248·6
18	10	776·1	·889862	·002455	4·748 „	167·1	167·95	246·9
19	20	771·4	·887279	·002583	4·994 „	165·5	166·30	245·3
20	30	767·0	·884795	·002484	4·803 „	163·9	163·7	243·7
21	40	762·8	·882411	·002384	4·610 „	162·5	163·2	242·2
22	50	758·6	·880013	·002398	4·637 „	161·0	161·75	240·7
23	2.00	754·6	·877717	·002296	4·440 „	159·5	160·25	239·2
24	10	750·7	·875466	·002251	4·353 „	158·2	158·85	237·8
25	20	746·9	·873263	·002203	4·260 „	156·9	157·55	236·5
26	30	743·1	·871047	·002216	4·285 „	155·7	156·30	235·3
27	40	739·5	·868938	·002109	4·079 „	154·5	155·10	234·1
28	50	735·9	·866819	·002119	4·097 „	153·4	153·95	232·9
29	3.00	732·2	·864630	·002190	4·233 „	152·3	152·85	231·8
30	10	729·0	·862728	·001902	3·680 „	151·2	151·77	230·8

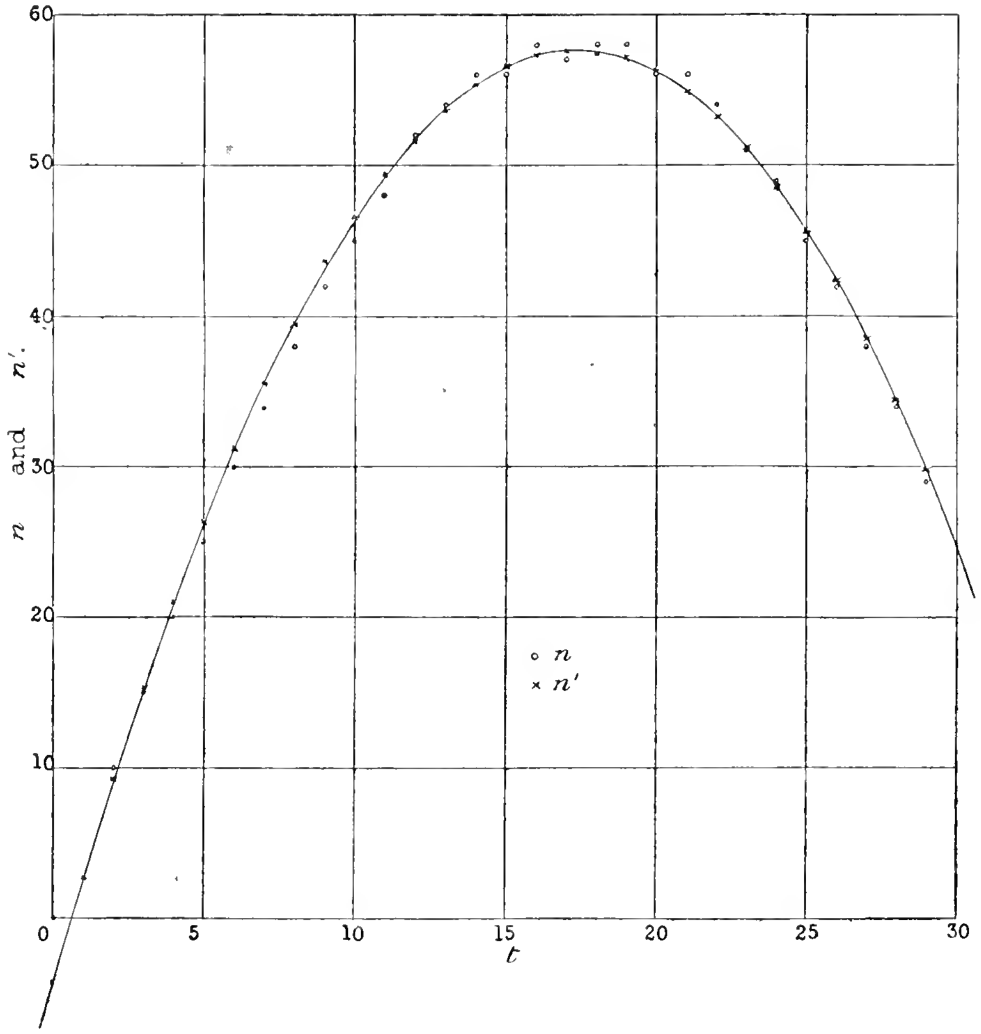
Specimen Page from Calculation Note-Book.

explained; and, the temperatures corresponding to the times being known, the emissivities can be referred to their respective temperatures.

29. Taking for an example the case of the results of April 2, 1906 (see table on p. 364, the times and the deflections (galvanometer readings) are given in Columns 1 and 3; and in Column 4 are given the logarithms of the deflections, while Column 5 contains the differences of these last, that is $\log v_0 - \log v$.* Noticing that the difference of logarithms is a number which increases as the experiment proceeds, and is a function of the time, to deal with the numbers conveniently we assume

$$\log v_0 - \log v = \mathrm{K}t + n,$$

choosing K by inspection so that Kt shall contain the greater part of the number which expresses $\log v_0 - \log v$; while n is a residue, as it were a correction on Kt, and obviously containing all the irregularities and the errors of experiment.



$$n' = \alpha + \beta t + \gamma t^2.$$

Silvered globe in vacuum = 0·06 M. April 2, 1906.

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* In the present investigation v_0 is the same as $(v_0 - \mathrm{V})$, and v is the same as $(v - \mathrm{V})$ of p. 358; that is, the present v_0 and v are the differences of temperatures, at times t_0 and t, between the cooling globe and the envelope.

The quantity n is now assumed to be of the parabolic form

$$n = \alpha+\beta t+\gamma t^2.$$

The justification for this assumption will be made clear presently from a comparison between observed and calculated values of n.

30. Returning, now, to the original forms, we have

$$-c\frac{dv}{dt} = e\mathrm{S}v \quad \text{and hence} \quad e = -\frac{c}{\mathrm{S}}.\frac{1}{v}.\frac{dv}{dt}.$$

But we have also

$$\log v_0 - \log v,$$

known by experiment, and equal to $\mathrm{K}t+n$; and we have, moreover,

$$\log_\epsilon v_0 - \log_\epsilon v = \mathrm{M}\,(\log v_0 - \log v),$$

where M is the modulus of the common logarithms.

Hence by differentiation, and comparison,

$$-\frac{1}{v}\frac{dv}{dt} = \frac{d}{dt}\mathrm{M}\,(\log v_0 - \log v)$$

$$= \mathrm{M}\frac{d}{dt}\{\mathrm{K}t+n\} = \mathrm{M}\,\{(\mathrm{K}+\beta)+2\gamma t\},$$

and, by substitution, we find

$$e = \frac{c\mathrm{M}}{\mathrm{S}t_1}\{(\mathrm{K}+\beta)+2\gamma t\};$$

t_1 (= 300) being introduced since K, α, β, γ, are in terms of 5 minutes as the unit of time.

Thus e is the emissivity when $t = 0$, plus or minus a quantity which, for want of a better name, we have been in the habit of calling "the time correction."

31. It now only remains to explain how n is dealt with, and how the values of α, β, and γ, are found. Referring again to the specimen page, on p. 364, and to Column 5, which contains the values of $\log v_0 - \log v$; the next column, Column 6, contains the values of Kt, K being chosen by inspection to be 25, so that when the values of Kt are subtracted from the corresponding numbers in the preceding Column 5, the remainders, shown in Column 7, shall be small and convenient for the process which is to follow. The numbers in Column 7 are sometimes even negative; experience directs the choosing of K. It is to be observed, also, that the factor 10^{-4} has been taken out of the numbers in Column 6. This must be kept in mind, and the factor inserted at the proper time, at the end of the calculations.

32. The next process is to form three simultaneous equations for the determination of α, β, and γ in the equation $\alpha+\beta t+\gamma t^2 = n'$. There are different ways in which this might be done, but perhaps the simplest way is to divide Column 7, containing n, into three equal parts, and construct columns containing the corresponding values of t

April 2, 1906. METHOD II.

Silvered Globe Cooling in Vacuum.

Vacuum Pressure = 0·06 **M**. Temperature of enclosure = – 194° C.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
t.	t^2.	Deflection.	Logarithm of deflection.	Log v_0 – log v.	Kt. K = 25.	Observed. n.	Calculated. n'.	$n - n'$.	Time correction.	Emissivity.	Difference of temperatures.	Absolute temperature of globe.
											$t-t'$ °C.	
0	0	867·1	2·9381	·0000	0	0	– 4·17	– 4·17	0	6·2103 × 10^{-6}	212·0	291°·0
1	1	861·0	·9350	31	25	6	2·74	+ 3·26	·07925	6·1311 ,,	208·3	287·3
2	4	855·1	·9321	60	50	10	9·24	+ 0·76	·15850	6·0518 ,,	204·8	283·8
3	9	849·4	·9291	90	75	15	15·31	– 0·31	·23775	5·9726 ,,	201·4	280·4
4	16	843·5	·9261	120	100	20	21·0	– 1·0	·31700	5·8933 ,,	198·1	277·1
5	25	837·7	·9231	150	125	25	26·3	– 1·3	·39625	5·8141 ,,	194·9	273·9
6	36	832·0	·9201	180	150	30	31·16	– 1·16	·47550	5·7348 ,,	191·8	270·8
7	49	826·3	·9172	209	175	34	35·62	– 1·62	·55475	5·6556 ,,	188·9	267·9
8	64	820·9	·9143	238	200	38	39·66	– 1·66	·63400	5·5763 ,,	186·2	265·2
9 **45**	81 **285**	815·4	·9114	267	225	42 **220**	43·30	– 1·3	·71325	5·4971 ,,	183·5	262·5
10	100	810·1	·9086	295	250	45	46·52	– 1·52	·79250	5·4178 ,,	181·0	260·0
11	121	804·9	·9058	323	275	48	49·36	– 1·36	·87175	5·3386 ,,	178·7	257·7
12	144	799·7	·9029	352	300	52	51·74	+ 0·26	·95100	5·2593 ,,	176·5	255·5
13	169	794·7	·9002	379	325	54	53·73	+ 0·27	1·03025	5·1801 ,,	174·4	253·4
14	196	789·8	·8975	406	350	56	55·32	+ 0·68	1·10950	5·1008 ,,	172·4	251·4
15	225	785·1	·8950	431	375	56	56·49	– 0·49	1·18875	5·0216 ,,	170·5	249·5
16	256	780·4	·8923	458	400	58	57·26	+ 0·74	1·26800	4·9423 ,,	168·8	247·8
17	289	776·0	·8899	482	425	57	57·61	– 0·61	1·34725	4·8631 ,,	167·1	246·1
18	324	771·4	·8873	508	450	58	57·56	+ 0·44	1·42650	4·7838 ,,	165·5	244·5
19 **145**	361 **2185**	767·0	·8848	533	475	58 **542**	57·10	+ 0·90	1·50575	4·7046 ,,	163·9	242·9
20	400	762·8	·8825	556	500	56	56·22	– 0·22	1·58500	4·6253 ,,	162·5	241·5
21	441	758·6	·8800	581	525	56	54·94	+ 1·06	1·66425	4·5461 ,,	161·0	240·0
22	484	754·6	·8777	604	550	54	53·24	+ 0·76	1·74350	4·4668 ,,	159·5	238·5
23	529	750·7	·8755	626	575	51	51·14	– 0·14	1·82275	4·3876 ,,	158·2	237·2
24	576	746·9	·8732	649	600	49	48·62	+ 0·38	1·90200	4·3083 ,,	156·9	235·9
25	625	743·1	·8711	670	625	45	45·67	– 0·67	1·98125	4·2291 ,,	155·7	234·7
26	676	739·5	·8689	692	650	42	42·36	– 0·36	2·06050	4·1498 ,,	154·5	233·5
27	729	735·9	·8668	713	675	38	38·61	– 0·61	2·13975	4·0706 ,,	153·4	232·4
28	784	732·3	·8647	734	700	34	34·46	– 0·46	2·21900	3·9913 ,,	152·3	231·3
29 **245**	841 **6085**	729·0	·8627	754	725	29 **454**	29·90	– 0·90	2·29825	3·9121 ,,	151·3	230·3

SPECIMEN PAGE FROM CALCULATION NOTE-BOOK.

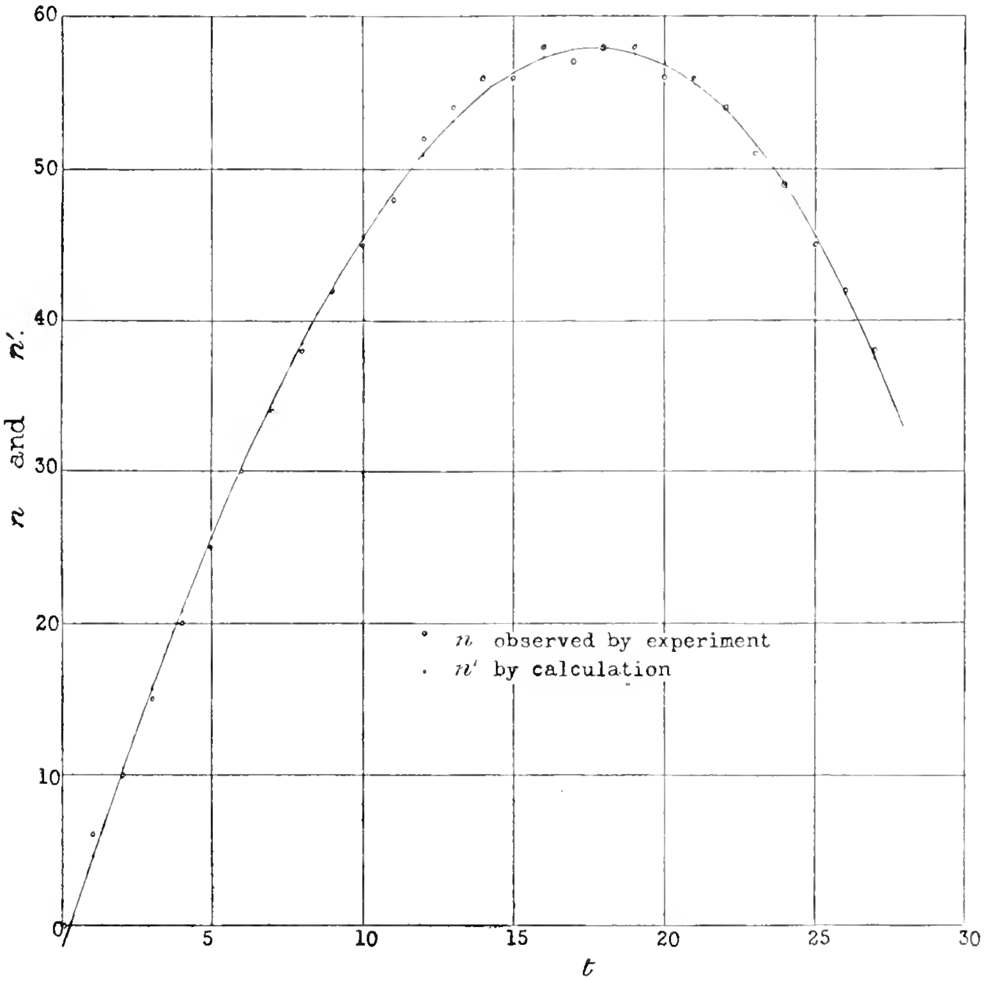
and t^2; to divide these columns similarly, then to take the sums of the numbers in each of the equal parts, and to use the respective sums as the values of n, t, and t^2, to form three equations. If this is done the equations become the following, as will be seen from the sums indicated in the specimen page, the coefficients of α being 10, as there are ten numbers in each of the three sums.

$$\begin{aligned} 10\alpha + 45\beta + 285\gamma &= 220, \\ 10\alpha + 145\beta + 2185\gamma &= 542, \\ 10\alpha + 245\beta + 6085\gamma &= 454. \end{aligned}$$

Solving these simultaneous equations, we find for the values of the three unknown quantities,

$$\alpha = -4{\cdot}175\,;\ \beta = 7{\cdot}115\,;\ \gamma = -0{\cdot}205.$$

33. Having determined the values of α, β, and γ, the next process is to find the series of values of n', which is done by putting the numerical values of t into the equation $n' = \alpha + \beta t + \gamma t^2$. The number n' is not required for the calculation of e, but is needed for comparison with n, and for verification of the exactness of the process. The values of βt and γt^2 are most easily obtained by means of CRELLE's Multiplication



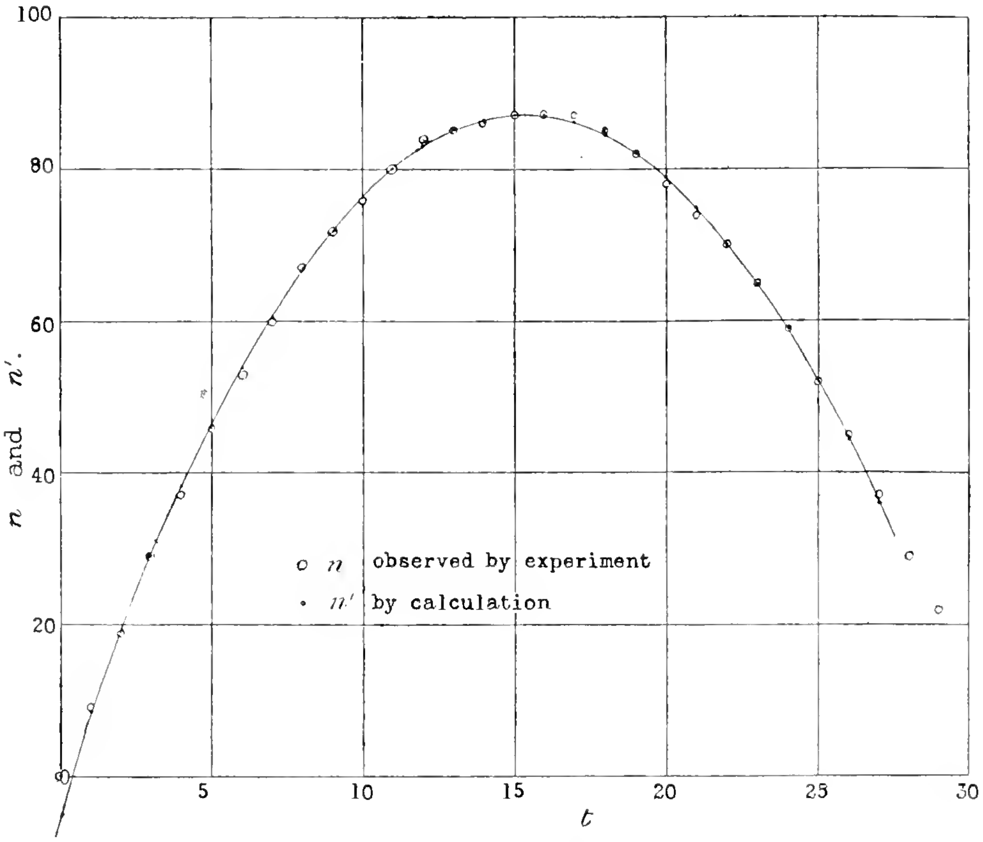
$n' = \alpha + \beta t + \gamma t^2 + \delta t^3.$

Silvered globe in vacuum = 0·06 M. April 2, 1906.

[In this diagram and the next one the small dots representing n' have not come out, as they lie on the curve.]

Tables. When calculated they are placed in suitable columns not shown in the specimen table, and from these columns the successive values of n' are obtained by addition, and they are placed in Column 8; while Column 9 gives the comparison between n and n'. Remembering that $n-n'$ has to be multiplied by 10^{-4}, it will be seen that the process of averaging leaves nothing to be desired.

34. An interesting experimental way of looking at this last question is to plot the values of n and n' on squared paper and to compare the curves. The results are shown in the accompanying diagrams, pp. 362, 365, 366; and the closeness of the agreement between the smooth and the unsmoothed curves is shown to the eye to be quite satisfactory. If it were not, the necessity for revision of the work would at once be revealed. In every case the plotted form of n and n' has been found to be obviously parabolic.



$n' = \alpha + \beta t + \gamma t^2 + \delta t^3$.

Sooted globe cooling in vacuum. September 18, 1906.

35. Column 10 contains the "time correction," as defined above. The numbers in this column are added to the emissivity at $t = 0$, which is the number that heads Column 11, and the sums thus obtained give the emissivities at times $t = 1$, $t = 2$, &c., &c. These emissivities are placed in Column 11; and opposite to them, in Column 12, the differences of temperatures between cooling body and surroundings at those times are shown; while, in Column 13, the corresponding absolute temperatures of the cooling globe are given.

Method 2a.

36. In some cases it was found desirable to use a fourth term, containing t^3, in the expression for n', when the formula stopping with t^2 did not give sufficient accuracy. This involved the finding of a fourth constant, δ. In this case $n' = \alpha+\beta t+\gamma t^2+\delta t^3$.

To calculate the emissivities the procedure is similar to that just described, except that four equations are formed for the determination of α, β, γ, δ; and by suitable modifications in the equations, p. 363, we find

$$e = \frac{\text{M}c}{\text{S}t_1}\{\text{K}+\beta+(2\gamma t+3\delta t^2)\};$$

the time correction, instead of being a linear quantity, containing a squared term. In most cases δ was negligible, and the first form of n' was found to be quite sufficient for our purpose.

DISCUSSION OF RESULTS.

37. The following tables contain the results of our experiments on radiation of heat at low temperatures. The tables are divided into three groups. The first group, Tables I. to VI. and XI., gives the loss of heat from a copper globe covered with a very fine coating of soot, hung in a spherical copper shell, also sooted, and at the highest vacuum. In this group, therefore, we have probably the nearest practicable approach to the case of a perfectly black body cooling in vacuum at very low temperatures.

38. In the second group, Tables VII. to X. and XII., all the circumstances are practically the same as in the first, except that the surface of the copper globe was covered with a coating of silver, polished to the highest degree to which we could attain.

39. The third group, Tables XIII. to XV., gives the cooling of a sooted globe, and of a highly polished silvered globe, in the same enclosure as is specified above, but in air at about standard pressure, and all at very low temperatures.

40. Tables I. and II. show the radiation from the sooted globe, at the highest vacuums we could reach, the temperature of the cooling globe being at the commencement about 10° C., and falling during the experiment, which lasted $2\frac{1}{2}$ hours, to $-59°$ C., the envelope being maintained at the temperature of liquid air during the whole time. These two tables are placed side by side in order that it may be seen to what extent agreement was found between experiments made at different dates, the circumstances being, as far as possible, repeated. The comparison shows that the exactness of agreement leaves nothing to be desired. Whatever there is of difference between the numbers obtained for the emissivity is certainly to be attributed to difference in the condition as to vacuum. This will be seen from comparisons among themselves of experiments at different vacuums.

41. It should be noted here that the vacuums attained in these experiments are certainly of a very much higher order than those obtained in Dr. BOTTOMLEY's older

experiments on this subject. The presence of the liquid air surrounding the enclosure causes condensation of any kind of collapsible vapour which might exist in the so-called vacuous space, *e.g.*, vapour of mercury, or any trace of vapour of water, &c., the existence of which would not be indicated by the M'Leod gauge, but which, should it exist, would certainly play its part in causing heat transference by convection.

42. Tables III., IV., V. give the emissivity from a sooted globe at a good vacuum, but less perfect than in the cases of Tables I. and II., and at gradually increasing pressure up to 60 **M.**, or about half-a-tenth of a millimetre.

43. The construction of the tables is clearly indicated by the headings. For each experiment there is given the condition of the surface, the vacuum pressure, and the temperature of the enclosure. In the second column is given the difference of temperatures between the globe and its surroundings at the time of the galvanometer reading. This difference, as has been stated, is obtained from the calibration curves of the thermojunctions. Column 3 gives the emissivity, calculated as has been explained and exemplified in Section 5 of the paper. Column 4 gives the absolute temperature of the globe at the moment of obtaining the galvanometer reading. Column 5 will be explained below. It contains what has been called "the radiation constant," calculated in accordance with STEFAN'S law.

44. Coming now to the tables of the second group, these give the emissivity for the highly polished silvered globe. Tables VII. and VIII. show the loss of heat at the highest vacuum we could obtain, with Sprengel pumps and cooled charcoal; and it will be seen that the loss from the sooted surface under these circumstances is four times as much as from the highly polished silvered surface at the same absolute temperatures of the cooling body and surroundings. This result quite agrees with those obtained in the earlier experiments of Dr. J. T. BOTTOMLEY.

Tables IX. and X. give the loss from a silvered surface in a less perfect vacuum. These, however, are of comparatively small interest.

45. Tables VI., XI., and XII., give the case of the silvered globe and of the sooted globe cooled to a temperature below that of the enclosure, and receiving heat by radiation from warmer surroundings.

Not many experiments of this kind have been made, so far as we are aware; but the results are interesting when considered in connection with the principle of "Heat Exchanges."

It may be noticed that in every case, both sooted and silvered, where the globe has been cooled below the temperature of its surroundings, and is allowed to rise in temperature by receiving heat from the walls of the enclosure, the calculated emissivity has turned out to be higher than in the reverse, and more ordinary, experiment. It is probable that this is due to deterioration of the vacuum, on account of the escape of gases or vapours from the surrounding walls on the removal of the liquid air. Such deterioration of the vacuum would not be indicated by the M'Leod gauge, as there is always a very considerable time lag in the readings of the gauge. Vacuum is very slowly transmitted from point to point along the connecting tubes which must intervene between the gauge and the space whose condition, as to vacuum, the gauge is to measure. In a foot-note, p. 352, this is referred to. The connecting tubes have been made as short as possible, but in spite of every care in this direction this inherent trouble has not been overcome.

46. The third group contains three tables which show the cooling of the copper globe in air at ordinary atmospheric pressure. In Table XIII. the copper globe is finely sooted; in Table XIV. the surface of the globe is silvered and brilliantly polished; while Table XV. gives the cooling of the globe with a silvered, but dull white surface.[*]

A comparison of these tables with the corresponding tables for the globes cooling in vacuum shows the part which is played by convection in the ordinary case of bodies cooling in air.

47. In the following short tables, the results of such a comparison for the cases of the sooted globe and the highly polished silvered globe are given. The emissivities[†] have been taken at corresponding temperatures for the globe cooling in vacuum, and cooling in air, for the two cases mentioned. These are placed opposite the temperatures to which they belong, and Column 1 of each table gives the absolute temperatures of the cooling globe. Column 2 gives the emissivity in vacuum Column 3 gives the number which corresponds to the emissivity in air; while Column 4 gives the ratios between the numbers in Column 3 and those in Column 2. The following points may be noticed with regard to the numbers in these tables. In the first place the relatively high numbers for the emissivity in air are very remarkable, and it is to be noticed that the numbers are very nearly the same for the sooted globe and the silvered globe. The true radiation goes almost for nothing in comparison with the loss due to radiation and convection combined.

1.	2.	3.	4.	1.	2.	3.	4.
Sooted globe.				Silvered globe.			
Absolute temperature.	e_1 in vacuum.	e_2 in air.	Ratio $\frac{e_2}{e_1}$.	Absolute temperature.	e_1 in vacuum.	e_2 in air.	Ratio $\frac{e_2}{e_1}$.
° C.				° C.			
284	$2 \cdot 152 \times 10^{-5}$	$3 \cdot 842 \times 10^{-4}$	17·85	270	$5 \cdot 368 \times 10^{-6}$	$3 \cdot 659 \times 10^{-4}$	68·2
260	$1 \cdot 948 \times 10^{-5}$	$3 \cdot 829 \times 10^{-4}$	19·6	260	$5 \cdot 045 \times 10^{-6}$	$3 \cdot 651 \times 10^{-4}$	72·4
240	$1 \cdot 714 \times 10^{-5}$	$3 \cdot 783 \times 10^{-4}$	22·1	240	$4 \cdot 115 \times 10^{-6}$	$3 \cdot 637 \times 10^{-4}$	88·4
220	$1 \cdot 393 \times 10^{-5}$	$3 \cdot 736 \times 10^{-4}$	26·8	230	$3 \cdot 501 \times 10^{-6}$	$3 \cdot 631 \times 10^{-4}$	103·4

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[*] This surface was caused by a fine deposit of mercury on the highly polished silvered surface.

[†] It is not in accordance with strict language to use the word "emissivity" in the case where air is present; but the lapse from strictness may be pardoned here for the sake of brevity.

48. The results of experiments made at the beginning of last century by Sir JOHN LESLIE and others seemed to show that the total loss of heat from a body cooling in dry air was made up of radiation and convection in about equal proportions. Such a statement as this is, however, very far from representing the state of the case with regard to loss of heat with full air pressure at very low temperatures. The loss by convection is enormously increased when the air is reduced in temperature nearly to liquefying point. On the other hand, the loss by pure radiation from the sooted globe at very low temperatures is extremely small; while the loss from the highly polished silvered globe is, so to speak, minute. Thus convection may be from 18 to 25 times the pure radiation from the sooted surface, instead of being about equal to it; while the convection is from 60 to 100 times the pure radiation from polished silver. We propose shortly to make some special experiments on this subject.

49. A question of great interest is the comparison of the results we have obtained, including Dr. BOTTOMLEY'S old results, with the 4th power law, or formula of STEFAN. According to STEFAN'S law, the emission, S, of heat from a "black" body is proportional to the 4th power of the absolute temperature of the cooling surface. Taking this law in conjunction with the law of "heat exchanges," the cooling of a "black" body at temperature θ in a "black" enclosure at temperature θ_0 ought to be proportional to the product of the "emission" and $(\theta^4-\theta_0^4)$; and may be represented by $\sigma\,(\theta^4-\theta_0^4)$, where σ is a constant, sometimes called "the radiation constant." In our tables it is not the "emission" of heat per square centimetre which is given, but the "emissivity," or the emission divided by the difference of temperatures between the cooling body and the surrounding envelope. If, then, e be the emissivity between θ and θ_0, we have $e = \mathrm{S}/(\theta-\theta_0)$; and, correspondingly, we shall have

$$\sigma = \frac{\mathrm{S}}{(\theta^4-\theta_0^4)} = \frac{e}{(\theta+\theta_0)\,(\theta^2+\theta_0^2)}.$$

We have applied this formula to all the tables where the cooling of the sooted globe is given, and where the vacuum is sufficiently good to make the experiment suitable for the purpose in hand. These numbers are given in Column 5 of the respective tables.

TABLES taken from 1893 Paper of J. T. BOTTOMLEY, for Comparison of Emissivities, and of STEFAN'S 4th Power Law.

	Oct. 22, 1889. Vacuum = 0·77 M. θ_0 Temp. of enclosure = 290°·5 abs.			Oct. 29, 1889. Vacuum = 0·45 M. θ_0 Temp. of enclosure = 288°·3 abs.			April 2, 1890. Vacuum = 0·8 M. θ_0 Temp. of enclosure = 289° abs.			April 8, 1890. Vacuum = 0·2 M. θ_0 Temp. of enclosure = 288° abs.		
	Emissivity.	Absolute temp. of globe.	Emission $/ (\theta^4 - \theta_0^4)$.	Emissivity.	Absolute temp. of globe.	Emission $/ (\theta^4 - \theta_0^4)$.	Emissivity.	Absolute temp. of globe.	Emission $/ (\theta^4 - \theta_0^4)$.	Emissivity.	Absolute temp. of globe.	Emission $/ (\theta^4 - \theta_0^4)$.
		θ			θ			θ			θ	
1	1·37 × 10^{-4}	370°·1	9·373 × 10^{-13}	1·25 × 10^{-4}	371°·9	8·551 × 10^{-13}	2·78 × 10^{-4}	512°·0	10·04 × 10^{-13}	2·23 × 10^{-4}	505°·5	8·30 × 10^{-13}
2	1·36 „	364·5		1·23 „	366·5		2·02 „	484·9		2·00 „	482·3	8·23 „
3	1·34 „	359·4	9·655 „	1·21 „	361·6	8·705 „	1·96 „	465·2	8·66 „	1·78 „	456·1	8·22 „
4	1·32 „	354·7		1·19 „	356·0		1·89 „	448·0		1·63 „	433·8	8·33 „
5	1·30 „	350·4	9·791 „	1·17 „	352·9	8·787 „	1·82 „	433·0	9·32 „	1·52 „	422·1	8·20 „
6	1·29 „	346·4		1·15 „	349·0		1·76 „	419·8		1·44 „	411·9	8·15 „
7	1·27 „	342·7	9·937 „	1·14 „	345·4	8·887 „	1·72 „	408·3	9·83 „	1·42 „	402·8	8·38 „
8	1·25 „	339·3		1·12 „	341·2		1·61 „	403·2		1·36 „	394·6	8·35 „
9	1·23 „	336·2	9·942 „	1·10 „	339·0	8·855 „	1·57 „	389·3	9·82 „	1·27 „	387·4	8·07 „
10	1·22 „	333·3		1·08 „	336·1		1·50 „	381·5		1·29 „	380·9	8·46 „
11	1·20 „	330·6	9·975 „	1·06 „	333·4	8·776 „	1·43 „	374·5	9·64 „	1·20 „	374·9	8·10 „
12	1·18 „	328·2		1·05 „	331·0		1·37 „	368·4		1·22 „	369·4	8·58 „
13	1·16 „	325·9	9·874 „	1·03 „	328·7	8·733 „	1·30 „	362·9	9·27 „	1·20 „	364·4	8·53 „
14	1·13 „	321·8		0·99 „	324·6		1·24 „	358·0	9·03 „	1·26 „	359·6	9·17 „
15	1·09 „	318·3	9·641 „	0·95 „	321·0	8·376 „				1·15 „	355·1	8·56 „
16	1·06 „	315·3								1·07 „	351·2	8·12 „
17	1·02 „	312·7	9·282 „									
18	0·989 „	310·5										
19	0·954 „	308·5	8·870 „									

NOTE.—*By Dr.* J. T. BOTTOMLEY.

Added July 11, 1907.—The foregoing paper contains an account of experiments on radiation of heat at very low temperatures, carried out by Mr. F. A. KING and the writer of the present note. From the results of these experiments we have calculated the thermal emissivity, from a carefully sooted surface, at the temperature stated. An attempt is made at the end of the paper to put these results into relation with the results of older experiments which I carried out fourteen years ago, with the same apparatus, and in precisely the same way, but at considerably higher temperatures. No comparison was, however, made in my former papers on this subject between the results of these experiments and what I may call the theoretical laws of thermal radiation, nor with the law of STEFAN deduced from the old experiments of DULONG and PETIT. The matter was entirely dealt with from an experimental point of view.

It seems desirable, now, that I should make an endeavour to compare our experimental results, as far as possible, both with STEFAN'S law and with results more recently obtained by other experimenters.

Careful experiments on thermal radiation have been made by WIEN and LUMMER, E. ST. JOHN, C. CHRISTIANSEN, LUMMER and PRINGSHEIM, and by F. KURLBAUM; but I find it very difficult to compare their results with my own. All my experiments have been made by the method of cooling, which gives directly, in absolute measure, the emissivity of the surface of the heated body. Almost all the other experimenters have used an indirect method, and have inferred the radiating power of the heated body from the indications of a bolometer or special form of thermojunction, determining the temperature to which this receptor is raised by the presence of the radiating body. In a paper by KURLBAUM[*] the experiments were carried on by means of the bolometer. The radiation was from the theoretical "black body" used by WIEN and LUMMER[†], *i.e.*, from the blackened interior of a hollow vessel, heated externally with steam, and having an opening in front through which the radiation passes; and the bolometer, placed opposite to the opening, receives the radiation. The transition from arbitrary to absolute units is difficult. The method is to find the temperature to which the bolometer rises, and at which it permanently stands, when at a given distance from the heated radiating body, and then to ascertain the amount of electric current which will keep the bolometer at this temperature. It seems difficult to put these two observations into sure relationship with each other, and to obtain the radiating power of the black body in absolute measure from experiments on the heat received by the cooler of the two bodies; but it is very interesting to find a close agreement between the results obtained by this indirect method and those obtained simply by directly measuring the

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[*] 'WIEDEMANN'S Annalen,' No. 65, 1898.

[†] 'WIEDEMANN'S Annalen,' No. 56, 1895, p. 451.

loss of heat from the warm radiator, particularly when it is considered how minute a proportion of the heat radiated in all directions falls upon the bolometer and is utilised for the measurement.

KURLBAUM also quotes in his paper the results of earlier investigators, but these experiments also are mostly indirect. Thus the results of LEHNEBACH are deduced with the help of a comparison between the radiating power of glass and that of the theoretical black body; and the same applies to those of GRAETZ. A result deduced from the work of KUNDT and WARBURG depends on the conducting power of gases for heat, while numbers quoted from CHRISTIANSEN are founded on considerations still more complicated.

In each case KURLBAUM deduces the emission (not emissivity) of heat by a body at 100° C. to a body at 0° C., or rather the heat received by a body at 0° C. from a "black" surface at 100° C. placed opposite to it. This is taken as the "emission" of heat between the absolute temperatures 273° C. and 373° C., and STEFAN'S coefficient is deduced from these numbers.

The following table is taken from KURLBAUM'S paper, except that I have interpolated Column 3. The results are in Gm. Cal./cm^2 × sec. :—

Observer.	$h_{100} - h_0$.	Average emissivity between 0° C. and 100° C.	STEFAN'S coefficient. σ.
LEHNEBACH, 1874	0·0152	$1{\cdot}52 \times 10^{-4}$	$11{\cdot}0 \times 10^{-13}$
KUNDT and WARBURG, 1875	0·014	$1{\cdot}4 \times 10^{-4}$	$10{\cdot}1 \times 10^{-13}$* $11{\cdot}1 \times 10^{-13}$
GRAETZ, 1880	0·0150	$1{\cdot}5 \times 10^{-4}$	$10{\cdot}8 \times 10^{-13}$
CHRISTIANSEN, 1883	0·0167	$1{\cdot}67 \times 10^{-4}$	$12{\cdot}1 \times 10^{-13}$
KURLBAUM, 1898	0·0176	$1{\cdot}76 \times 10^{-4}$	$12{\cdot}8 \times 10^{-13}$†

In calculating the results of my experiments, following my original plan, I am not led to tabulate "emissions" but "emissivities." Hence my figures do not compare directly with those placed in the column of this table under the heading $h_{100} - h_0$. For this reason I have interpolated Column 3, which shows what may be taken to be the average *emissivity* between the temperatures 100° C. and 0° C. For comparison with these numbers I may quote the following table, compiled from my paper in the 'Phil. Trans.' for 1893. The numbers are taken out of tables giving emissivities at different, but extremely low, pressures.

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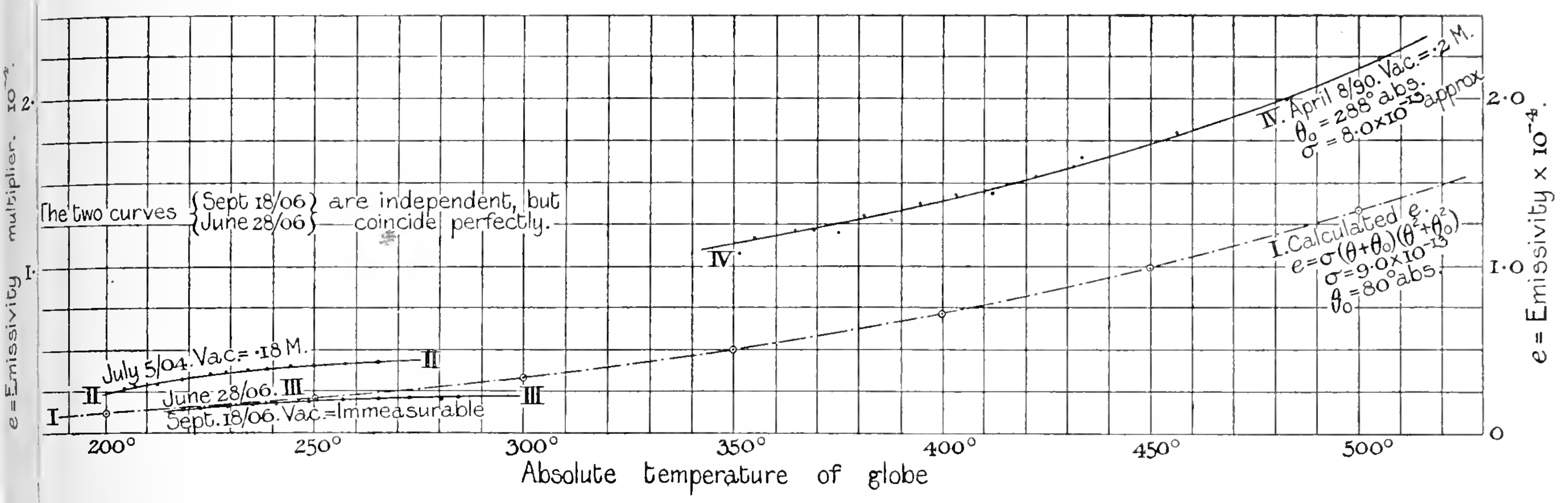
* The number 10·1 is reckoned by using the value 0·014 as the emission between $h_{100} - h_0$, as given above; 11·1 is a number obtained by GRAETZ from the data given by KUNDT and WARBURG.

† This number seems to be considered as final by KURLBAUM. I find that he makes use of it in subsequent papers as an accepted figure, *e.g.*, 'WIED. Ann.', Band 2, 1900, p. 550; and others quote it as authoritative. See, *e.g.*, POYNTING, 'Phil. Trans.', 1904, p. 526, and POYNTING and THOMSON, 'Heat.'

Date.	Vacuum.	Temperature of globe.	Temperature of enclosure.	Emissivity (defined).	Emission divided by $(\theta^4 - \theta_0^4)$.
	M.	°C.	°C.		
October 22, 1889 . .	0·77	97·0	17·5	$1·37 \times 10^{-4}$	$9·373 \times 10^{-13}$
		63·0		$1·23 \times 10^{-4}$	$9·94 \times 10^{-13}$
		45·0		$1·09 \times 10^{-4}$	$9·64 \times 10^{-13}$
October 29, 1889 . .	0·45	99·0	15·3	$1·25 \times 10^{-4}$	$8·55 \times 10^{-13}$
		72·0		$1·14 \times 10^{-4}$	$8·89 \times 10^{-13}$
		56·0		$1·03 \times 10^{-4}$	$8·73 \times 10^{-13}$
April 2, 1890 . . .	0·8	116·0	16·0	$1·57 \times 10^{-4}$	$9·82 \times 10^{-13}$
		101·5		$1·43 \times 10^{-4}$	$9·64 \times 10^{-13}$
		85·0		$1·24 \times 10^{-4}$	$9·03 \times 10^{-13}$
April 8, 1890 . . .	0·2	96·4	15·0	$1·22 \times 10^{-4}$	$8·58 \times 10^{-13}$
		86·6		$1·26 \times 10^{-4}$	$9·17 \times 10^{-13}$
		78·2		$1·07 \times 10^{-4}$	$8·12 \times 10^{-13}$

From these tables, given complete on p. 371, I have extracted numbers corresponding to temperatures between the limits 0° C. and 100° C. It will be seen that the values I have obtained for STEFAN'S coefficient are also lower than those which they have obtained at similar temperatures; but my numbers do not differ so much from the results of GRAETZ and KUNDT and WARBURG as do those of CHRISTIANSEN and KURLBAUM from the results of the last-named observers.

The accompanying sheet of curves brings out some of the relations of the numbers under consideration in a somewhat interesting way. Taking the Stefan coefficient to be 9×10^{-13}, and taking the temperature of a sooted enclosure such as I used in my experiments to be 80° absolute, I have calculated corresponding emissivities; and on plotting these they form curve I. on the sheet. To compare these with emissivities obtained by experiment, I have laid down the results of the experiments of Mr. KING and myself of dates July 5, 1904, and June 28, September 18, 1906. In each case the surrounding envelope was at the temperature of liquid air. In one case the vacuum was 0·18 **M.**, and in the other it was absolutely unmeasurable, and as nearly perfect as can be obtained by the use of charcoal and liquid air. I have also traced the curve for my old results of April 8, 1890, where the temperature of the enclosure was 15° C., or 288° absolute, and the vacuum was 0·2 **M.** Now comparing the curves for July 5 and September 18, it will be seen that the emissivity in the case of the former at 0·18 **M.** is rather more than double that at the nearly perfect vacuum; and it seems not unnatural to suppose that, if I had been able to improve correspondingly the vacuum of April 8, the emissivity would have been reduced to less than half of that which I found. I have other evidence that this supposition is very close to the truth. If the circumstances under which this 1890 experiment was carried out had been precisely comparable with those represented by curves II. and III., it seems almost sure that the emissivity found would have been very close to that shown on curve I.



At the present time, Mr. KING and I are endeavouring to make arrangements for carrying out experiments on the cooling of a sooted body, very much on the same lines as those on which we have been working, but with the cooling globe heated at the commencement to a temperature considerably above that of boiling water, and with the enclosure kept all the time at the temperature of liquid air. In our experiments up till now we have only been able to work, as it were, piecemeal and in sections; first, from the high temperature down to say 15° C., and then from 15° on to the lower temperature of liquid air. An experiment through the long range, and with the enclosure kept at the temperature of liquid air, would give data suitable for direct comparison with curve III.

It may be, however, that after all a copper globe sooted is not a true "black" body, no matter how carefully prepared. One point, among others, on which there seems great uncertainty in this connection, is the question of conduction of heat from the surface of the copper to the sooty covering. This was a difficulty with the late Sir GEORGE STOKES, who discussed it with me on more than one occasion.

I am preparing comparative experiments to test my sooted globe against the artificial black body.

Details of Separate Experiments.

Group I.—Sooted Globe Cooling in Vacuum.

I.
September 18, 1906.
Copper globe finely sooted.*
Vacuum pressure immeasurable on M'Leod gauge.
Temperature of enclosure = 79°·5 absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.	Emission $\dfrac{\quad}{\theta^4-\theta_0^4}$.
	° C.		°	
1	193·1	2·064 × 10^{-5}	272·6	7·270 × 10^{-13}
2	189·6	2·035 ,,	269·1	7·414 ,,
3	183·1	1·976 ,,	262·6	7·673 ,,
4	174·3	1·889 ,,	253·8	8·012 ,,
5	166·6	1·802 ,,	246·1	8·274 ,,
6	159·7	1·714 ,,	239·2	8·484 ,,
7	153·6	1·626 ,,	233·1	8·575 ,,
8	148·2	1·539 ,,	227·7	8·613 ,,
9	143·1	1·452 ,,	222·6	8·603 ,,
10	138·7	1·363 ,,	218·2	8·489 ,,

II.
June 28, 1906.
Copper globe finely sooted.
Vacuum pressure = 0·03 **M.**
Temperature of enclosure = 79° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.	Emission $\dfrac{\quad}{\theta^4-\theta_0^4}$.
	° C.		°	
1	194·9	2·021 × 10^{-5}	273·9	7·047 × 10^{-13}
2	181·5	1·922 ,,	260·5	7·640 ,,
3	170·6	1·824 ,,	249·6	8·098 ,,
4	165·8	1·775 ,,	244·8	8·284 ,,
5	161·2	1·726 ,,	240·2	8·456 ,,
6	153·0	1·627 ,,	232·0	8·710 ,,
7	149·3	1·578 ,,	228·3	8·799 ,,
8	142·4	1·480 ,,	221·4	8·918 ,,
9	139·4	1·430 ,,	218·4	8·914 ,,
10	136·5	1·381 ,,	215·5	8·901 ,,

III.
July 5, 1904.
Copper globe sooted.
Vacuum pressure = 0·18 **M.**
Temperature of enclosure = 80° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.	Emission $\dfrac{\quad}{\theta^4-\theta_0^4}$.
	° C.		°	
1	185·2	4·217 × 10^{-5}	265·2	15·92 × 10^{-13}
2	170·0	3·985 ,,	250·0	17·53 ,,
3	164·2	3·870 ,,	244·2	18·08 ,,
4	158·7	3·755 ,,	238·7	18·68 ,,
5	154·0	3·639 ,,	234·0	18·95 ,,
6	145·4	3·407 ,,	225·4	19·50 ,,
7	138·2	3·176 ,,	218·2	19·72 ,,
8	132·3	2·945 ,,	212·3	19·57 ,,
9	127·3	2·713 ,,	207·3	19·13 ,,
10	124·7	2·598 ,,	204·7	18·89 ,,

IV.
June 21, 1906.
Copper globe finely sooted.
Vacuum pressure = 8·0 **M.**†
Temperature of enclosure = 80° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.	Emission $\dfrac{\quad}{\theta^4-\theta_0^4}$.
	° C.		°	
1	201·1	4·827 × 10^{-5}	281·1	
2	192·5	4·767 ,,	272·5	
3	184·8	4·707 ,,	264·8	
4	171·0	4·588 ,,	251·0	
5	158·9	4·469 ,,	238·9	
6	153·3	4·409 ,,	233·3	
7	143·4	4·290 ,,	223·4	
8	134·7	4·170 ,,	214·7	
9	127·2	4·052 ,,	207·2	
10	123·7	3·992 ,,	203·7	

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* Copper globe with same coating of soot as in experiment of June 28, 1906.

† Copper enclosure leaking slightly.

Group I.—Sooted and Silvered Globes Cooling in Vacuum (continued).

V.
May 31, 1905.
Copper globe sooted.
Vacuum pressure = 60 M.*
Temperature of enclosure = 81° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.
	° C.		
1	209·6	$8\cdot914\times10^{-5}$	290°·6
2	165·4	8·559 ,,	246·4
3	133·0	8·029 ,,	214·0
4	118·6	7·675 ,,	199·6
4	107·0	7·322 ,,	188·0
6	97·8	6·968 ,,	178·8
7	86·3	6·438 ,,	167·3
8	76·5	5·908 ,,	157·5
9	68·1	5·378 ,,	149·1
10	63·3	5·023 ,,	144·3

VI.
September 18, 1906.
Copper globe finely sooted.
Increasing in temperature.
Vacuum pressure immeasurable on M'Leod gauge.
Temperature of enclosure = 291°·8 absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.
	° C.		
1	60·6	$3\cdot742\times10^{-5}$	231°·2
2	56·2	3·947 ,,	235·6
3	52·1	4·153 ,,	239·7
4	47·9	4·358 ,,	243·9
5	44·1	4·564 ,,	247·7
6	40·4	4·769 ,,	251·4
7	36·8	4·975 ,,	255·0
8	33·4	5·181 ,,	258·4
9	30·3	5·386 ,,	261·7
10	25·7	5·728 ,,	266·1

XI.
July 5, 1904.
Copper globe sooted.
Increasing in temperature.
Vacuum pressure = 1·8 M.
Temperature of enclosure = 287° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.
	° C.		
1	75·8	$6\cdot092\times10^{-5}$	211°·2
2	70·2	6·261 ,,	216·8
3	64·7	6·430 ,,	222·3
4	59·6	6·597 ,,	227·4
5	54·8	6·766 ,,	232·2
6	50·0	6·934 ,,	237·0
7	45·7	7·103 ,,	241·3
8	41·7	7·271 ,,	245·3
9	37·7	7·440 ,,	249·3
10	31·0	7·778 ,,	256·0

XII.
July 21, 1905.
Silvered globe highly polished.
Increasing in temperature.
Vacuum pressure = 0·1 M.
Temperature of enclosure = 294° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.
	° C.		
1	16·9	$9\cdot206\times10^{-6}$	277°·1
2	16·7	9·296 ,,	277·3
3	16·5	9·382 ,,	277·5
4	16·3	9·470 ,,	277·7
5	16·1	9·556 ,,	277·9
6	15·95	9·645 ,,	278·05
7	15·75	9·734 ,,	278·25
8	15·38	9·908 ,,	278·62
9	15·0	10·083 ,,	279·0
10	14·61	10·258 ,,	279·39

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* The copper enclosure was leaking slightly and consequently the vacuum pressure was variable. The average pressure was 60 M.

GROUP II.—Silvered Globe Cooling in Vacuum.

VII.
March 23, 1906.
Silvered globe highly polished.
Vacuum pressure = 0·05 M.
Temperature of enclosure = 81° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. *e*.	Absolute temperature of globe. θ.
	° C.		
1	207·3	5·812 × 10^{-6}	288°·3
2	197·3	5·581 ,,	278·3
3	188·4	5·349 ,,	269·4
4	181·0	5·118 ,,	262·0
5	174·7	4·887 ,,	255·7
6	169·1	4·655 ,,	250·1
7	164·4	4·424 ,,	245·4
8	160·1	4·191 ,,	241·1
9	156·2	3·960 ,,	237·2
10	150·3	3·565 ,,	231·3

Globe has not been polished since July 20, 1905. In the meantime it has been hanging within the enclosure, which was exhausted.

VIII.
April 2, 1906.
Silvered globe highly polished.
Vacuum pressure = 0·06 M.
Temperature of enclosure = 79° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. *e*.	Absolute temperature of globe. θ.
	° C.		
1	212·0	6·210 × 10^{-6}	291°·0
2	201·4	5·972 ,,	280·4
3	191·8	5·734 ,,	270·8
4	183·5	5·497 ,,	262·5
5	176·5	5·259 ,,	255·5
6	170·5	5·021 ,,	249·5
7	165·5	4·783 ,,	244·5
8	161·0	4·545 ,,	240·0
9	156·9	4·308 ,,	235·9
10	152·3	3·991 ,,	231·3

IX.
July 20, 1905.
Silvered globe very highly polished.
Vacuum pressure = 0·1 M.
Temperature of enclosure = 79° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. *e*.	Absolute temperature of globe. θ.
	° C.		
1	211·0	4·027 × 10^{-6}	290°·0
2	207·5	3·990 ,,	286·3
3	203·7	3·953 ,,	282·7
4	200·4	3·917 ,,	279·4
5	197·0	3·879 ,,	276·0
6	193·8	3·842 ,,	272·8
7	190·7	3·805 ,,	269·7
8	187·8	3·768 ,,	266·8
9	184·2	3·719 ,,	263·2
10	181·0	3·670 ,,	260·0

Globe repolished before this experiment.

X.
July 11, 1905.
Silvered globe tarnished surface.
Vacuum pressure = 20 M.
Temperature of enclosure = 79° absolute.

No.	Difference of temperatures. $(t-t')$° C.	Emissivity. *e*.	Absolute temperature of globe. θ.
	° C.		
1	215·0	5·178 × 10^{-5}	294°·0
2	175·3	5·022 ,,	254·3
3	151·3	4·867 ,,	230·3
4	139·6	4·764 ,,	218·6
5	134·6	4·713 ,,	213·6
6	121·3	4·557 ,,	200·3
7	110·5	4·402 ,,	189·5
8	101·4	4·247 ,,	180·4
9	93·5	4·092 ,,	172·5
10	76·0	3·679 ,,	155·0

GROUP III.—Sooted and Silvered Globes in Air.

XIII. June 22, 1906. Sooted globe in air. Barometer pressure = 765·5 millims. Temperature of enclosure = 80° absolute.				XIV. October 9, 1906. Silvered globe highly polished.* Barometer pressure = 758 millims. Temperature of enclosure = 80° absolute.				XV. April 12, 1906. Silvered globe with dull surface.† Barometer pressure = 761·7 millims. Temperature of enclosure = 80° absolute.			
No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.	No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.	No.	Difference of temperatures. $(t-t')$° C.	Emissivity. e.	Absolute temperature of globe. θ.
	° C.		°		° C.		°		° C.		°
1	208·6	$3\cdot874 \times 10^{-4}$	288·6	1	190·8	$3\cdot658 \times 10^{-4}$	270·8	1	204·0	$3\cdot671 \times 10^{-4}$	284·0
2	171·4	3·805 ,,	251·4	2	160·4	3·637 ,,	240·4	2	174·0	3·634 ,,	254·0
3	143·6	3·738 ,,	223·6	3	135·9	3·617 ,,	215·9	3	143·6	3·576 ,,	223·6
4	110·4	3·625 ,,	190·4	4	116·5	3·597 ,,	196·5	4	110·0	3·482 ,,	190·0
5	82·0	3·490 ,,	162·0	5	72·0	3·530 ,,	152·0	5	83·4	3·369 ,,	163·4
6	62·7	3·355 ,,	142·7	6	59·5	3·503 ,,	139·5	6	59·7	3·218 ,,	139·7
7	46·6	3·187 ,,	126·6	7	45·8	3·462 ,,	125·8	7	45·3	3·040 ,,	125·3
8	29·3	3·047 ,,	109·3	8	32·8	3·372 ,,	112·8	8	29·6	2·866 ,,	109·6
9	15·2	2·837 ,,	95·2	9	17·0	3·188 ,,	97·0	9	17·6	2·614 ,,	97·6
10	6·1	2·509 ,,	86·1	10	8·2	2·958 ,,	88·2	10	2·2	1·574 ,,	82·2
Dry air let into the enclosure, June 21, 1906.											

$(t-t')$ is the difference of temperatures between globe and its surroundings in degrees Centigrade.

e is the emissivity, or loss of heat, per square centimetre per second per 1° C. of difference of temperature.

$$\text{STEFAN's coefficient} = \frac{\text{emission}}{\theta^4-\theta_0{}^4} = \frac{\text{emissivity}}{(\theta^2+\theta_0{}^2)\,(\theta+\theta_0)}.$$

---

* The enclosure was removed at the end of this experiment, and the silvered globe was found to be just as bright as when hung in position. Globe repolished on October 8, 1906.

† When the enclosure was opened at the conclusion of this experiment, the silvered globe had a dull white surface due to condensation of mercury vapour upon the globe.

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SERIES A, VOL. 208, pp. 381–443.
[PLATES 30–31.]

BAKERIAN LECTURE.

THE EFFECTS OF TEMPERATURE AND PRESSURE ON THE THERMAL CONDUCTIVITIES OF SOLIDS.—PART II.

THE EFFECTS OF LOW TEMPERATURES ON THE THERMAL AND ELECTRICAL CONDUCTIVITIES OF CERTAIN APPROXIMATELY PURE METALS AND ALLOYS.

BY

CHARLES H. LEES, D.Sc., F.R.S.,
PROFESSOR OF PHYSICS IN THE EAST LONDON COLLEGE, UNIVERSITY OF LONDON.

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XI. BAKERIAN LECTURE.—*The Effects of Temperature and Pressure on the Thermal Conductivities of Solids.—Part II.*[*] *The Effects of Low Temperatures on the Thermal and Electrical Conductivities of Certain Approximately Pure Metals and Alloys.*

By CHARLES H. LEES, *D.Sc., F.R.S., Professor of Physics in the East London College, University of London.*

Received November 8,—Read in Abstract December 12, 1907,—Received in Revised Form, with Additions, March 24, and Read as Bakerian Lecture, March 26, 1908.

[PLATES 30–31.]

DURING the last fifty years a considerable amount of attention has been bestowed on the question of the variations of the thermal and electrical conductivities of metals with the temperature, but the results obtained by different observers, especially of thermal conductivities, differed so widely from each other that the answer to the thermal part of the question long remained doubtful.[†] In recent years, however, there has been an accumulation of evidence in favour of a slight decrease of thermal conductivity with increase of temperature from 0° C. to 100° C. in the case of most of the metals. The experiments of LORENZ,[‡] and more especially the careful work of JÄGER and DIESSELHORST,[§] have contributed greatly to this result. In both these cases the experiments were limited to the range of temperature between 0° C. and 100° C., and it seemed advisable, in view of the importance of both questions in the electronic theories of conduction of heat and electricity in metals, to extend the range over which the theories could be tested, particularly in the direction of low temperatures, where the experiments of DEWAR and FLEMING[‖] had already furnished information as to the electrical conductivities. The present paper contains an account of the measurements of the thermal and electrical conductivities carried out for this purpose.

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[*] Part I., "The Effect of Temperature on the Thermal Conductivities of some Electrical Insulators," appeared in the 'Philosophical Transactions,' A, vol. 204, pp. 433–466 (1905).

[†] A good account of the subject will be found in GRAETZ's article in the new edition (1906) of WINKELMANN'S 'Handbuch der Physik,' Band III.

[‡] L. LORENZ, 'Ann. der Physik,' 13, p. 422 (1881).

[§] W. JÄGER and H. DIESSELHORST, 'Abh. d. Phys.-Techn. Reichsanstalt,' 3, p. 269 (1900).

[‖] J. DEWAR and J. A. FLEMING, 'Phil. Mag.,' 36, p. 271 (1893).

and the results obtained. The first section deals with measurements of the thermal, the second with measurements of the electrical, conductivities of certain metals and alloys, and the third section compares the results with the electronic theories.

SECTION I.—THE THERMAL CONDUCTIVITY MEASUREMENTS.

Outline of Method Used.

When the thermal conductivity of a substance which conducts heat readily has to be determined, it is advisable to give the material the form of a wire or thin rod and to allow the heat to flow along the axis. By this arrangement it is easy to insure that the difference of temperature to be measured is not too small, and it has been a favourite one with observers. Sometimes the rod has been exposed to the air of the room, as in the original experiments of BIOT,* sometimes enclosed in a vessel as in those of WIEDEMANN and FRANZ.† As the present experiments were to be carried out at temperatures down to that of liquid air, the former method could not be used without entailing an excessive loss of heat from the sides of the rods. The method of enclosure was therefore adopted.

The scale of the apparatus was mainly determined by the necessity of lowering its temperature to that of liquid air and maintaining it at that temperature. This leads to a reduction in the size of the rods, and must be compensated by an increase in the accuracy of the heat and temperature measurements. This was secured by communicating the heat to one end of the rod and measuring it electrically, and by determining the difference of temperature at two points of the rod by means of two platinum thermometers.

The Apparatus.

The metal rods used, R, fig. 1, were circular cylinders 7 to 8 centims. long, ·585 centim. in diameter, and were accurately turned out of larger rods. In use they were placed vertically, the lower end fitting into a copper disc, D, of 2·69 centims. diameter, 1·2 centims. thick in the centre, 1 centim. thick at the circumference, which in its turn fitted accurately into the lower end of a copper cylinder, T, of 2·69 centims. internal, 3·32 centims. external, diameter, 9·5 centims. long, closed at the top.

On the rod three thin brass sleeves,‡ A, B, and C, 0·66 centim. long, were placed, the fit being of such a nature that the sleeves could be slid along the rod with the fingers without the application of more than a small force.§

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* J. B. BIOT, 'Traité de physique' (1816).

† G. WIEDEMANN and R. FRANZ, 'Ann. der Phys.,' 89, p. 497 (1853).

‡ I had not succeeded at this date in making thin mica rings which would stand the wear of use with the whole of the rods, see p. 428.

§ For the accurate turning and fitting of the rods and sleeves I am indebted to Mr. E. T. COOK, the Mechanician of the University of Manchester.

The outer surface of each ring was covered with shellac varnish, thinly dusted with fine marble powder, and the ring then allowed to dry. On the top of this insulating layer, in the case of the sleeve C, a No. 40 single silk-covered platinoid wire, 30·6 centims. long, was wound, so that the winding occupied the middle portion of the sleeve, leaving a margin of 0·13 centim. at each end. On the insulating layer of each of the two sleeves A and B an equal length of single silk-covered No. 40 pure platinum wire* was similarly wound. The ends of the fine platinoid wire were soldered to the ends of two 55-centim. lengths, L, of No. $22\frac{1}{2}$ double silk-covered and shellac-varnished copper wire, and the ends of the fine platinum wire to two 48-centim. lengths, M or N, of the same copper wire. To obviate stress on the fine wires, the copper wires of each sleeve were placed in parallel grooves in the edge of a thin disc of wood, W, attached to the sleeve by a few turns of silk thread, *s*, wound round the sleeve, wood and wires. In each case a total length of 1·5 centims. of the thin wire used was required to make connections to the ends of the copper leads, the remaining length, 29·1 centims., being actually wound on the sleeve.

The three sets of copper leads passed out of the copper enclosure through three holes in the thin part of the copper disc, which formed the bottom of the enclosure. At the holes extra insulation was provided for the wires, and they could be fixed in position with respect to the disc by three small wedges of wood placed in the holes of the disc.

The copper enclosure was supported on a wire frame, F, by means of which it could be placed in a straight Dewar tube, V, of 4·2 centims. internal diameter, 25 centims. internal depth, so that the bottom of the enclosure was 2 centims. above the bottom of the tube.

The copper leads were brought up to the mercury switch arrangements described on p. 384, by means of which the difference of the resistances of the two platinum coils and the actual resistance of one of them could be found. The current supplied to the heating coil, and the EMF at its terminals, were measured as described on p. 384.

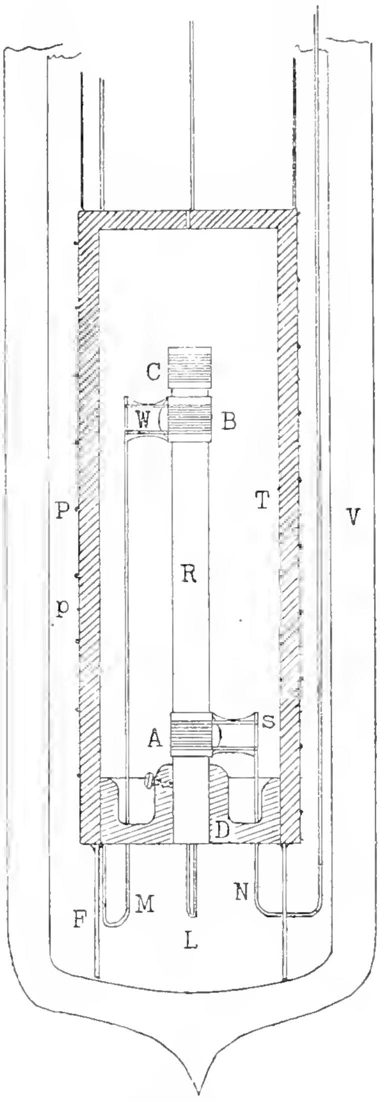

Fig. 1.

Around the outside of the copper tube an insulated platinoid wire, *p*, having the same resistance as that of the fine platinoid wire of the heating coil, C, was wound, and whenever the current was switched off the heating coil on the rod, it was switched on to that of the tube, so that the amount of heat supplied to the apparatus should be the same throughout an experiment. In addition, a further coil, P, was wound on

---

* Obtained specially from Messrs. JOHNSON, MATTHEY & Co.

the outside of the tube to allow the temperature of the tube, if necessary, to be rapidly raised.

The Resistance Bridge.

The mercury switch to which the leads from the platinum resistance coils were brought was so arranged that when the difference of resistance of the coils was to be found, they formed two of the arms of a resistance bridge, the other two arms of which consisted of two coils, of about 2 ohms each, of manganin wire wound together and adjusted to equality to within 1 part in 10,000. A dial resistance with mercury contacts, allowing a variation of resistance from 0 to 0·10 ohm in steps of 0·01 ohm, could be placed in series with either of the platinum resistance coils in the bridge, and provided the adjustment necessary for balancing the bridge approximately. The resistance required to give an accurate balance was calculated from the deflections of the galvanometer for the two values of the dial resistance nearest to the balance value. As the leads to the two platinum coils were made as nearly as possible equal to each other, the resistance so found is the difference between the resistances of the two coils. Similarly, when the resistance of one of the coils was to be determined, that coil was, by means of the mercury switch, made one arm of a resistance bridge of which the two equal manganin coils formed two other arms, and the fourth consisted of a resistance box giving 10 ohms in steps of 0·1 ohm, and the 0·01-ohm dial in series. The leads again being as nearly as possible equal, the resistance of the fourth arm, when the bridge was balanced, was equal to the resistance of the platinum coil.

The current used in balancing the bridge was derived from a Leclanché cell connected to the bridge through a resistance of 53 ohms. The connections of the cell could be reversed if necessary.

The galvanometer was of the moving-coil type, and had a resistance of 22 ohms. It could be used either with or without a shunt of 10 to 50 ohms, as occasion required.

The bridge key was a thermo-electric one which, in its normal position, disconnects the cell from the bridge, but leaves the galvanometer connected, and, when depressed, disconnects the galvanometer for an instant, connects the cell, then re-connects the galvanometer. By this means thermo-electric effects in the bridge have no influence on the observations.

Method of Experimenting.

In setting up the apparatus for an experiment, the rod, sleeves, and edges of the copper disc forming the base of the tube were smeared with olive oil, and the joints between rod and base of tube, between rod and sleeves, and between the base of the tube and the tube itself, made in such a way that the oil excluded all air. Good thermal contacts were thus secured. None of these contacts come in the direct line of flow of heat within the region of measurement, but they influence certain small corrections, to be considered presently. Before the rod was placed finally in the tube the leading wires from the coils were wedged in the holes at the base, and the distances apart of the three sleeves measured to 0·01 centim. The apparatus when fitted together was lowered into the Dewar tube, the connections made, and after a few minutes, during which the temperature throughout became uniform, the differences, if any, between the resistances of the platinum wires were measured.

An electric current was then sent round the heating coil on the rod, and was adjusted so that a suitable difference of resistance between the upper and lower platinum coils was obtained. The heating current was then switched from rod to tube, and after 5 to 10 minutes the difference of resistance of the platinum coils, and the actual resistance of the lower coil, were found.

If a second observation, taken 3 to 5 minutes later, gave a different value for the difference of resistance, a further interval of 3 to 5 minutes was allowed and the difference again tested, and this was repeated till the difference of resistance became constant. The current supplied to the heating coil and the E.M.F. at its terminals were then read, and the current switched from tube to rod.

After 5 to 10 minutes the difference of resistance of the platinum coils was again found, and observations taken till it remained constant. The resistance of the lower coil was then measured, and the current in the heating coil and the E.M.F. at its terminals read; then the current was again switched from rod to tube and the measurements repeated.

The mean of the two differences of resistance found when the heating current flowed round the tube, subtracted from the difference found when the heating current flowed round the rod, gives, so long as the rate of rise of temperature of the apparatus is regular, the difference of resistance which would be produced if the heating current were supplied to the rod and the temperature of the tube were kept constant (see p. 397).

The Dewar tube was then filled with liquid air and, when the apparatus had cooled down to the temperature of liquid air, the remaining liquid was poured out by tilting the tube.

Observations of difference of resistance between the platinum coils, with the heating current round the tube, were then made as before till the difference became steady, the resistance of one coil was determined, and the heating current and voltage measured. The current was then switched from tube to rod, and the observations repeated. In this way observations with the heating current alternately round rod and tube were made throughout the gradual rise of temperature of the apparatus from that of liquid air to some temperature above that of the air of the room, the rate of rise of temperature being, if necessary, increased by a constant electric current sent through the supplementary heating coil wound on the copper tube.

Theory of the Apparatus.

If a thin rod of uniform cross section is entirely surrounded by a vessel kept at constant temperature, and has heat supplied to it near one end, while the other is in good thermal contact with the wall of the vessel, the distribution of temperature within the rod, from its point of contact with the vessel to that at which the heat is supplied, will be represented by the equation

$$v = \frac{\mathrm{Q}}{(phqk)^{1/2}} \sinh \left(\frac{ph}{qk}\right)^{1/2} x \Big/ \cosh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where v is the excess of temperature of the rod at the cross section situated x centims. from the end of the rod in contact with the vessel, over that of the vessel, p is the perimeter, and q the area of cross section of the rod, h the heat lost per second from 1 sq. centim. of the surface of the rod when its temperature exceeds that of the enclosing vessel by 1° C., k is the thermal conductivity of the rod, and Q is the amount of heat which crosses the section of the rod at any point x_{C} per second.

In calculating Q from the energy supplied and the heat lost from the surface of the bar beyond x_{C}, we may, if the point x_{C} is near the free end of the rod, and the heat is supplied to the rod at a uniform rate between x_{C} and the free end, take the mean temperature of the surface of the bar between x_{C} and the end to be identical with the temperature $v_{\mathrm{C}'}$ which would be observed at $x_{\mathrm{C}'}$, a point which divides the distance between x_{C} and the end, in the ratio 1 : 2 if the above equation for v held throughout the heated portion of the rod.* If s is the area of the surface of the bar beyond x_{C}, and H is the total heat supplied to the bar,

$$\mathrm{Q} = \mathrm{H} - shv_{\mathrm{C}'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence

$$v = \mathrm{H} \sinh \left(\frac{ph}{qk}\right)^{1/2} x \Big/ \left[(phqk)^{1/2} \cosh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}} + hs \sinh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}'} \right]. \quad . \quad . \quad (3)$$

If the temperature excesses v_{A} and v_{B} at two sections x_{A} and x_{B} are observed, then

$$\frac{\mathrm{H}}{v_{\mathrm{B}} - v_{\mathrm{A}}} = (phqk)^{1/2} \cosh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}} + hs \sinh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}'} \Big/ \left[\sinh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{B}} - \sinh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{A}} \right].$$

Hence

$$\frac{\mathrm{H}}{v_{\mathrm{B}} - v_{\mathrm{A}}} \left[x_{\mathrm{B}} \sinh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{B}} \Big/ \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{B}} \quad - x_{\mathrm{A}} \sinh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{A}} \Big/ \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{A}} \right]$$

$$= qk \cosh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}} + hsx_{\mathrm{C}'} \sinh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}'} \Big/ \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}'}$$

and

$$k = \left[\frac{\mathrm{H}}{v_{\mathrm{B}} - v_{\mathrm{A}}} (x_{\mathrm{B}}\mathrm{S}_{\mathrm{B}} - x_{\mathrm{A}}\mathrm{S}_{\mathrm{A}}) - hsx_{\mathrm{C}'}\mathrm{S}_{\mathrm{C}'} \right] \Big/ q \cosh \left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}}, \quad . \quad . \quad . \quad . \quad (4)$$

---

* This ratio is exact if the loss of heat from one square centimetre of the surface of the bar may be neglected in comparison with the heat generated per square centimetre.

where S_A, &c., are written for the functions $\sinh (ph/qk)^{1/2} x_A/(ph/qk)^{1/2} x_A$, &c., whose values for small values of the denominators do not differ much from 1.

From this equation k may be calculated if an approximate value of it is known and is substituted in the hyperbolic functions which involve it. In the experiments to be described these functions have values not differing greatly from unity. A sufficiently close approximation to the value of k for this substitution may, in fact, be found by putting

$$\sinh (ph/qk)^{1/2} x \Big/ \left(\frac{ph}{qk}\right)^{1/2} x = \cosh \left(\frac{ph}{qk}\right)^{1/2} x = 1.$$

The effect of temperature on the dimensions of the rods is neglected, as it does not appear likely to influence the value of the conductivity found by so much as 1 part in 300.

In the actual apparatus the heat was supplied to the rod by the passage of the electric current through a platinoid wire wound on an independent sleeve placed on the bar, and the temperatures were measured by the resistances of platinum wires wound on similar sleeves.* It is therefore necessary to determine the effect of the sleeves on the result previously given.

Effect of the Sleeves.

Let v be the excess of temperature of the rod and v' that of the sleeve at points in a plane perpendicular to the axis of the rod, distant x from the central transverse section of the sleeve, the isothermal surfaces being assumed, as in the previous calculation, to be planes perpendicular to the axis.†

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* See note, p. 382.

† The distribution of temperature v throughout a rod of length $2l$, radius R, and conductivity k, which receives heat at a uniform rate h per square centimetre per second through a strip of breadth b of its curved surface at one end, and loses it at a corresponding strip at the other end and at no other point, is given by the equation

$$v = \frac{8hl}{k\pi^2} \sum_{m=0}^{\infty} (-1)^m \frac{1}{(2m+1)^2} \sin (2m+1) \frac{\pi b}{2l} \sin (2m+1) \frac{\pi x}{2l} \, I_0\left(\overline{2m+1}\,\frac{\pi r}{2l}\right) \Big/ I_1\left(\overline{2m+1}\,\frac{\pi R}{2l}\right),$$

where x is the distance of a point from the central transverse section of the rod, r its distance from the axis, and I_0 and I_1 Bessel functions for unreal arguments.

The mean temperature $\bar{v}$ over a strip of the surface of the rod of breadth b, whose centre is a from the central transverse section, is given by

$$\bar{v} = \frac{16Hl^2}{k\pi^4 b^2 R} \Sigma (-1)^m \frac{1}{(2m+1)^3} \sin (2m+1) \frac{\pi b}{2l} \sin (2m+1) \frac{\pi b}{4l} \sin (2m+1) \frac{\pi a}{2l} \, I_0\left(\overline{2m+1}\,\frac{\pi R}{2l}\right) \Big/ I_1\left(\overline{2m+1}\,\frac{\pi R}{2l}\right),$$

where $H = h 2\pi b R$ is the total flow of heat.

If the heat were generated at a uniform rate throughout the material of the rod within the distance b of the end, the flow of heat would be linear and the temperature at a would be given by

$$v = \frac{16Hl^2}{k\pi^4 b R^2} \Sigma (-1)^m \frac{1}{(2m+1)^3} \sin (2m+1) \frac{\pi b}{2l} \sin (2m+1) \frac{\pi a}{2l}.$$

A comparison of the numerical values of the first few terms of the two series, in the case of the shortest rod used, shows that even in that case the error committed in assuming the isothermal surfaces in the rod to be plane is not so large as 1 in 500, Let q, q' be the areas of cross section of rod and sleeve respectively, p, p' their outer perimeters, and k, k' the conductivities of their materials.

The thickness t'' and conductivity k'' of the thin layer of olive oil between rod and sleeve are small enough compared to those of the rod and sleeve to allow the heat conducted through the layer parallel to the axis of the rod to be neglected. The heat conducted across a length dx of the layer from rod to sleeve in 1 second is equal to $pk''(v-v')\,dx/t''$.

We have then the following equations for the steady distribution of temperature in rod and sleeve :—

In rod

$$qk\frac{d^2v}{dx^2}-\frac{pk''}{t''}(v-v')=0. \qquad (5)$$

In sleeve

$$q'k'\frac{d^2v'}{dx^2}+\frac{pk''}{t''}(v-v')-p'hv'=0. \qquad (6)$$

The last term of the second of these equations is small and may be neglected.*

Taking the temperature at the central transverse section to be zero, we have as the solutions of equations (5) and (6)

$$(qk+q'k')\,v=\mathrm{H}_0\left(x+\frac{q'k'}{qk}\frac{1}{\alpha}\frac{\sinh\alpha x}{\cosh\alpha b}\right), \qquad (7)$$

$$(qk+q'k')\,v'=\mathrm{H}_0\left(x-\frac{q'k'}{qk}\frac{1}{\alpha}\frac{\sinh\alpha x}{\cosh\alpha b}\right), \qquad (8)$$

where H_0 is the flow of heat through the central transverse section of rod and sleeve, and

$$\alpha^2=\frac{pk''}{t''}\left(\frac{1}{qk}+\frac{1}{q'k'}\right).$$

If b' = the length of free rod equivalent in thermal resistance to the length b of rod enclosed by sleeve, we have

$$b'=b\frac{qk}{qk+q'k'}\left\{1+\frac{q'k'}{qk}\frac{\tanh\alpha b}{\alpha b}\right\}. \qquad (9)$$

To determine whether any further simplification is possible, we note that in the apparatus used the constants have the following values :—

b = 0·33 centim., q = 0·268 sq. centim., qk = 0·011 to 0·27 according to the rod used, q' = 0·088 sq. centim., k' = 0·17 to 0·27 according to the temperature, $q'k'$ = 0·015 to 0·024, k'' = 0·0004, t'' = 0·0012 centim., and p = 1·84 centims.

Hence αb lies between 3·2 and 1·7.

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* The error introduced by neglecting h in estimating b', the length of free rod equivalent in thermal resistance to the length b of rod enclosed by sleeve, is about 1 per cent. in the worst case, *i.e.*, that of the shortest rod and lowest conductor. The error produced in the determination of k is about ·1 per cent.

Thus tanh ab will vary between the limits 0·997 and 0·936, having the former value in the case of the worst conducting rods at low temperatures, and the latter in the case of good conducting rods at high temperatures. The error in the estimate of b', if we write tanh $ab = 1$, will even in the latter case only amount to 3 per cent., and the error in k due to it will not exceed 0·04 per cent.

We have, then, the simplified equation

$$b' = \frac{qk}{qk+q'k'}b + \frac{q'k'}{qk+q'k'}\frac{1}{a},$$

or

$$b' = \frac{qk}{qk+q'k'}b + \frac{q'k'}{qk+q'k'}\left[\frac{pk''}{t''}\left(\frac{1}{qk}+\frac{1}{q'k'}\right)\right]^{-1/2}$$

$$= \frac{qk}{qk+q'k'}b + \left(\frac{q'k'}{qk+q'k'}\right)^{3/2}\left(\frac{t''}{pk''}qk\right)^{1/2} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The first term on the right is obviously the correction due to the increase of cross section at the sleeve, and the second that due to the ends of the sleeve, at which the flow does not immediately take advantage of the increase of section.

We have seen that in the above equation k varies from ·04 to 1·0 according to the rod under test, while k' varies from 0·17 at 100° to 0·27 at 300° absolute. Hence qk varies from 0·011 to 0·27 according to the rod, and $q'k'$ from 0·015 at 100° to 0·024 at 300° absolute.

The variation of k' with temperature has, however, only a very small effect on the value of b', as will be seen from the following table of values for $k' = 0·17$ and 0·27.

VALUES of b' in centimetres.

k.	For $k' = 17$.	For $k' = 27$.	For mean k'.	k.	For $k' = 17$.	For $k' = 27$.	For mean k'.
·03	·176	·161	·168	·17	·282	·272	·277
·05	·213	·195	·204	·22	·291	·283	·287
·07	·235	·219	·227	·27	·297	·290	·294
·09	·250	·235	·242	·50	·312	·308	·310
·11	·261	·249	·255	1·00	·321	·318	·320
·14	·274	·262	·268				

If for simplicity of calculation we take the mean value of b' as holding throughout the whole range of temperature for any single bar, we make an error in the calculation of k which will not exceed 0·4 per cent. even in the case of the worst conductor tested, LIPOWITZ's alloy, and will be insignificant for most of the other materials.

Thus we have the following values for x_A, x_B and x_C of the formula (4) for k :—

$x_A = a_1+b'$, where a_1 = distance from enclosure to near edge of first sleeve.

$x_B = x_A+2b'+a_2 = a_1+a_2+3b'$, where a_2 = distance between the near edges of first and second sleeves.

$x_C = x_B+b'+a_3 = a_1+a_2+a_3+4b'$, where a_3 = distance between the near edges of second and third sleeves.

$x_{C'} = x_C+\frac{2}{3}b' = a_1+a_2+a_3+4{\cdot}7b'$.

a_1 and a_3 were in every case made 0·10 centim.

Estimation of the Small Difference of Temperature between the Rod and the Platinum Resistance Coils.

In addition to a slight difference between the temperature v_0 of the rod and that of the sleeve, v'_0, at the central transverse section of the sleeve, there is a further slight difference between the latter and that of the wire of the platinum resistance v''_0, which may both be calculated with sufficient accuracy for the present purpose by taking

$$pk''\frac{v_0-v'_0}{t''} = p'k'''\frac{v'_0-v''_0}{t'''} = p''hv''_0,$$

where $p = 1{\cdot}84$ centims. is the perimeter, $t'' = 0{\cdot}0012$ centim. the thickness, $k'' = 0{\cdot}0004$ the conductivity, of the layer of oil between the rod and sleeve, $p' = 2{\cdot}14$ centims. the perimeter, $t''' = 0{\cdot}014$ centim. the mean thickness,[*] $k''' = 0{\cdot}0006$ the conductivity, of the layer of silk and shellac between sleeve and wire, and $p'' = 2{\cdot}28$ centims. the perimeter of the outer surface of the wire.

From the above we obtain

$$v_0 = (1+29h)\,v''_0.$$

Within the range of temperature covered by the experiments h varies from 0·00016 at 110° absolute to 0·00027 at 300° absolute. Taking the mean value 0·00022 as sufficient for the present purpose, we find

$$v_0 = 1{\cdot}006v''_0. \quad \ldots\ldots\ldots\ldots \quad (11)$$

In the work which follows, the mean temperature of the platinum coil wound on the sleeve so as to cover 0·4 centim. of its length is taken as identical with the temperature at the centre of its length, the difference between the two being too small to influence the results appreciably.

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[*] Obtained from the minimum thickness, 0·012 centim., by the addition of a correction suggested by MAXWELL'S 'Electricity and Magnetism,' I., p. 280. The thermal conductivities are only known roughly, so that the final value of the correcting term is not likely to be very accurate. Its influence on the values of the conductivities is, however, very small.

Corrections due to the Leads to the Platinum Resistance Coils.

It has been stated (p. 383) that only 29·1 centims. of the total length, 30·6 centims., of platinum wire were actually wound on the sleeve; the remainder, 1·5 centims., served to make connection to the No. 22½ double silk-covered copper wires leading to the resistance bridge.

Owing to its comparatively large cross section the whole of the copper wire may be assumed to have the temperature of the enclosure, but the temperature in each 0·8 centim. of platinum wire will vary from that of the enclosure to that of the coil of which it is the continuation. This will make the mean temperature of the wire as determined by its resistance slightly less than the temperature of that part of it on the sleeve, and will also lead to the conduction of a small amount of heat from the rod to the leads. We have therefore to determine the magnitude of these effects.

If we measure x along the platinum wire from its junction with the copper wire, we have for the temperature excess v at x the equation

$$v = v''_0 \frac{\sinh \alpha x}{\sinh \alpha l},$$

where v''_0 is, as before, the temperature of the wire on the sleeve, and $\alpha = \left(\frac{ph}{qk}\right)^{1/2}$, where p is the perimeter, q the cross section, of the wire, k the conductivity of its material, and h the external conductivity.

The mean value $\bar{v}$ of v is given by

$$\bar{v} = v''_0 \frac{\cosh \alpha l - 1}{\alpha l \sinh \alpha l} = v''_0 \frac{\sinh \frac{1}{2}\alpha l}{\alpha l \cosh \frac{1}{2}\alpha l} = \frac{v''_0}{2} \frac{\sinh \frac{1}{2}\alpha l}{\frac{1}{2}\alpha l} \Big/ \cosh \tfrac{1}{2}\alpha l.$$

For the platinum wire used, p measured over the silk $= 0·046$ centim., $h = 0·00022$ (mean), $q = 0·00012$ sq. centim., $k = 0·166$; therefore $\alpha = \left(\frac{101}{199}\right)^{1/2} = 0·71$, and $l = 0·8$ centim. Hence

$$\tfrac{1}{2}\alpha l = 0·28 \quad \text{and} \quad \bar{v} = \frac{v''_0}{2} \frac{1·013}{1·039} = 0·487 v''_0.$$

The resistance of the wire will therefore be the same as if, at each end of it, the length on the sleeve were increased by $l' = 0·487 l = 0·365$ centim. and the projecting ends removed. The effective length of the wire as used is, therefore, not the total length, 30·6 centims., but a shorter length, 29·83 centims. Hence

temperature excess of wire on sleeve = 30·6/29·83 = 1·026 times mean temperature excess of whole wire.

Hence, in the original equation for k ((4), p. 386), we must take

$$(v_A, v_B) = (1+29h)(v''_A, v''_B)$$

and

$$(v''_A, v''_B) = 1·026 (\bar{v}_A, \bar{v}_B),$$

where $\bar{v}_A$ and $\bar{v}_B$ are the mean temperatures over the whole of each platinum wire. Hence we have as the connection between the temperature of the rod and the observed temperature of the platinum wires,

$$(v_A,\ v_B) = (1{\cdot}026+29h)\,(\bar{v}_A,\ \bar{v}_B)\ \text{mean value.} \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

The amount of heat conducted from the sleeve* along the wire at its point of contact with the sleeve is equal to the value of $qk\,(dv/dx)$ at $x = 1$, which is

$$qkv''_0\alpha\frac{\cosh\alpha l}{\sinh\alpha l} = \frac{qkv''_0}{l}\cosh\alpha l\Big/\frac{\sinh\alpha l}{\alpha l} = \frac{qkv''_0}{l}\,\frac{1{\cdot}161}{1{\cdot}053}$$
$$= \frac{0{\cdot}00012\times0{\cdot}166}{0{\cdot}8}\,1{\cdot}12v''_0 = 0{\cdot}000028v''_0.$$

For the two platinum wires of the upper sleeve this amounts to $0{\cdot}000056v_0''$, which must be deducted from the heat supplied to give the heat which flows down the rod to the platinum thermometers.

Corrections for Leads in Power Circuit.

As in the case of the platinum resistance coils, so in that of the heating coil, the No. 40 platinoid wire constituting it was not wholly wound on the sleeve, but at each end 0·8 centim. projected and served to make contact with the No. $22\frac{1}{2}$ copper wires supplying current to the coil. Part, therefore, of the difference of potential measured was expended on the leads and on that part of the platinoid wire not on the sleeve. On the other hand, the passage of the current through the latter portion of the wire raised its temperature above that of the wire on the sleeve, and some of the heat generated in it would in consequence reach the sleeve by conduction along the wire. We require to determine this amount.

If W watts are spent in the platinoid wire, and L is the total length of the wire, $\frac{W}{4{\cdot}19L}$ gram-degrees of heat are generated per second in each centimetre of the wire. The equation for the distribution of temperature excess v along the wire in the steady state will therefore be

$$qk\frac{d^2v}{dx^2}+\frac{W}{4{\cdot}19L}-phv = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

where q, k, p, h have the usual meanings.

The solution of this equation may be put in the form

$$\left(\frac{W}{4{\cdot}19Lph}-v\right)\sinh\left(\frac{ph}{qk}\right)^{1/2}l$$
$$= \left(\frac{W}{4{\cdot}19Lph}-V_L\right)\sinh\left(\frac{ph}{qk}\right)^{1/2}(l-x)+\left(\frac{W}{4{\cdot}19Lph}-v''_{C'}\right)\sinh\left(\frac{ph}{qk}\right)^{1/2}x, \quad . \qquad (14)$$

---

* The amount conducted from the sleeve through the wooden support of the leads was too small to be taken into account.

where V_L is the temperature at the junction of the platinoid wire with the copper lead, $v''_{C'}$ that of the wire on the sleeve, x is measured from the copper lead, and l is the length of the platinoid wire between the copper lead and the sleeve.

If we neglect the heat generated by the current in the copper lead, and suppose the length of the lead to be sufficient for its temperature excess to fall to zero before the wire emerges from the containing tube, its temperature excess v_1 at a point $-x$ from the junction with the platinoid is given by the equation

$$v_1 = V_L \exp. \left(\frac{p_1 h}{q_1 k_1}\right)^{1/2} x,$$

where p_1, h_1, q_1, k_1 refer to the copper wire and have the usual meanings.

Since the flow of heat at the copper-platinoid junction is continuous, we must have, at $x = 0$,

$$qk\frac{dv}{dx} = q_1 k_1 \frac{dv_1}{dx},$$

i.e.,

$$\Big\{(phqk)^{1/2}\Big/\sinh\left(\frac{ph}{qk}\right)^{1/2} l\Big\}\Big\{\left(\frac{W}{4{\cdot}19Lph}-V_L\right)\cosh\left(\frac{ph}{qk}\right)^{1/2} l-\left(\frac{W}{4{\cdot}19Lph}-v''_{C'}\right)\Big\}=(p_1 h q_1 k_1)^{1/2}V_L.$$

Hence

$$V_L = \Big\{\frac{W}{4{\cdot}19Lph}\Big[\cosh\left(\frac{ph}{qk}\right)^{1/2} l-1\Big]+v''_{C'}\Big\}\Big/\Big\{\cosh\left(\frac{ph}{qk}\right)^{1/2} l+\left(\frac{p_1 q_1 k_1}{pqk}\right)^{1/2}\sinh\left(\frac{ph}{qk}\right)^{1/2} l\Big\}.$$

The flow of heat out of the exposed platinoid wire into the sleeve is given by the value of

$$-qk\frac{dv}{dx} \text{ at } x = l,$$

i.e., by

$$\Big\{(phqk)^{1/2}\Big/\sinh\left(\frac{ph}{qk}\right)^{1/2} l\Big\}\Big\{-\left(\frac{W}{4{\cdot}19Lph}-V_L\right)+\left(\frac{W}{4{\cdot}19Lph}-v''_{C'}\right)\cosh\left(\frac{ph}{qk}\right)^{1/2} l\Big\}$$

$$= \Big\{(phqk)^{1/2}\Big/\sinh\left(\frac{ph}{qk}\right)^{1/2} l\Big\}$$

$$\Bigg\{-\Big[\frac{W}{4{\cdot}19Lph}-\Big\{\frac{W}{4{\cdot}19Lph}\Big(\cosh\left(\frac{ph}{qk}\right)^{1/2} l-1\Big)+v''_{C'}\Big\}\Big/\Big\{\cosh\left(\frac{ph}{qk}\right)^{1/2} l+\left(\frac{p_1 q_1 k_1}{pqk}\right)^{1/2}\sinh\left(\frac{ph}{qk}\right)^{1/2} l\Big\}\Big]$$

$$+\left(\frac{W}{4{\cdot}19Lph}-v''_{C'}\right)\cosh\left(\frac{ph}{qk}\right)^{1/2} l\Bigg\}.$$

The total flow into the sleeve from the two wires will therefore be

$$= 2\Big\{(phqk)^{1/2}\Big/\sinh\left(\frac{ph}{qk}\right)^{1/2} l\Big\}$$

$$\Bigg\{-\Big\{\frac{W}{4{\cdot}19Lph}\Big[\left(\frac{p_1 q_1 k_1}{pqk}\right)^{1/2}\sinh\left(\frac{ph}{qk}\right)^{1/2} l+1\Big]+v''_{C'}\Big\}\Big/\Big\{\cosh\left(\frac{ph}{qk}\right)^{1/2} l+\left(\frac{p_1 q_1 k_1}{pqk}\right)^{1/2}\sinh\left(\frac{ph}{qk}\right)^{1/2} l\Big\}$$

$$+\left(\frac{W}{4{\cdot}19Lph}-v''_{C'}\right)\cosh\left(\frac{ph}{qk}\right)^{1/2} l\Bigg\} \quad . \qquad (15)$$

For the platinoid wire the values of the constants are $q = 0{\cdot}00012$ sq. centim., $k = 0{\cdot}050$ (mean), $p = 0{\cdot}046$ centim. over silk, $h = 0{\cdot}00022$ (mean).

Hence

$$\left(\frac{ph}{qk}\right)^{1/2} = (1{\cdot}67)^{1/2} = 1{\cdot}29,\ \left(\frac{ph}{qk}\right)^{1/2} l = 1{\cdot}03,\ (pqk)^{1/2} = 5{\cdot}2 \times 10^{-4}, \text{ and } (phqk)^{1/2} = 78 \times 10^{-7}.$$

$$4{\cdot}19\mathrm{L}ph = 1{\cdot}31 \times 10^{-3}.$$

For the copper wire, $q_1 = 0{\cdot}0033$ sq. centim., $k_1 = 1{\cdot}00$ (mean), $p_1 = 0{\cdot}27$ centim. over silk.

Hence

$$(p_1 q_1 k_1)^{1/2} = (9 \times 10^{-4})^{1/2} = 0{\cdot}030.$$

The flow of heat into the sleeve from the two wires per second will therefore be

$$= 0{\cdot}0060\mathrm{W} - 0{\cdot}000020 v''_{\mathrm{C}'}.$$

Thus of W watts spent in the wire, only

$$\left(\frac{29{\cdot}0}{30{\cdot}6} + 0{\cdot}0060\right)\mathrm{W} - 0{\cdot}000020 v''_{\mathrm{C}'},$$

i.e.,

$$0{\cdot}954\mathrm{W} - 0{\cdot}000020 v''_{\mathrm{C}'}$$

reach the sleeve, where $v''_{\mathrm{C}'}$ is the excess of the mean temperature of the sleeve over that of the surrounding tube.

The watts were measured at the ends of the copper leads, for the resistance of which a further correction must be made, a correction which will depend on the temperature of the leads and therefore of the tube. Each lead of copper wire, 0·065 centim. diameter, was 55 centims. long, and of this length 33 centims. was in the Dewar tube, 22 centims. in air. The resistance per metre at the temperature of the air, 15° to 18° C., may be taken as 0·051 ohm, and the total resistance of the leads as 0·056 ohm at the temperature of the air. When the platinum temperature of the Dewar tube is τ, we may, with sufficient accuracy, take the resistance of the leads to be

$$0{\cdot}056\left(\frac{2}{5} + \frac{3}{5}\frac{\tau}{290}\right) \text{ ohm}$$

$$= 0{\cdot}022 + 0{\cdot}000116\tau.$$

If, therefore, A amperes flow through the coil, and give a difference of potential of P volts at the terminals, the watts W spent in the platinoid wire

$$= \mathrm{A}\,\{\mathrm{P} - (0{\cdot}022 + 0{\cdot}000116\tau)\,\mathrm{A}\}.$$

Hence the watts expended on the sleeve

$$= 0{\cdot}954\mathrm{A}\,\{\mathrm{P} - (0{\cdot}022 + 0{\cdot}000116\tau)\,\mathrm{A}\} - 0{\cdot}000020 v''_{\mathrm{C}'}, \quad . \quad . \quad . \quad (16)$$

where $v''_{\mathrm{C}'}$ is the excess of the mean temperature of the sleeve over that, τ, of the tube.

It has been stated that the power supplied was measured by an ammeter in circuit and by applying a voltmeter to the ends of the heating coil for the few seconds necessary to take a reading. Owing to the resistance of the voltameter, $R_1 = 113$ ohms at 14° C., not being very great compared to that of the heating coil, $R_0 = 6{\cdot}4$ ohms at 18° C., the measured value P_0 of the volts at the ends of the heating coil is less than the value P when the voltameter is not in circuit, and the readings obtained must, if r is the resistance external to the coil, and the electromotive force in circuit is constant, be multiplied by

$$\frac{R_0+R_1}{R_1}\,\frac{r+R_0R_1/(R_0+R_1)}{r+R_0}$$

to give the true volts on the coil, *i.e.*,

$$\text{the volts P on the coil} = P_0\left(1+\frac{R_0}{R_1}\right)\left(1-\frac{R_0^2}{(R_0+R_1)\,(r+R_0)}\right).$$

Since the current was derived throughout from three storage cells kept well charged, it will be sufficient in the factor involving r to write $r+R_0 = 6/A$, and we have

$$\text{volts P on coil} = P_0\left(1+\frac{6{\cdot}4}{113}\right)\left(1-\frac{(6{\cdot}4)^2}{119{\cdot}4\times 6}A\right) = 1{\cdot}057P_0\,(1-0{\cdot}057A).$$

Hence the watts spent on the sleeve

$$\begin{aligned}&= 0{\cdot}954A\,\{1{\cdot}057\,(1-0{\cdot}057A)\,P_0-(0{\cdot}022+0{\cdot}000116\tau)\,A\}-0{\cdot}000020v''_{C'}\\ &= 1{\cdot}008A\,\{(1-0{\cdot}057A)\,P_0-(0{\cdot}021+0{\cdot}00011\tau)\,A\}-0{\cdot}000020v''_{C'}.\end{aligned}$$

Hence H, the total quantity of heat imparted to the bar per second, is given by the equation*

$$4{\cdot}19H = 1{\cdot}008A\,\{(1-0{\cdot}057A)\,P_0-(0{\cdot}021+0{\cdot}00011\tau)\,A\}-0{\cdot}000020v''_{C'}-0{\cdot}000056v''_{B}.$$

Or, since $(v''_B,\ v''_C) = (v_B,\ v_C)$ very nearly,

$$4{\cdot}19H = 1{\cdot}008A\,\{(1-0{\cdot}057A)\,P_0-(0{\cdot}021+0{\cdot}00011\tau)\,A\}-0{\cdot}000020v_{C'}-0{\cdot}000056v_{B}.$$

Hence

$$H = 0{\cdot}2406A\,\{(1-0{\cdot}057A)\,P_0-(0{\cdot}021+0{\cdot}00011\tau)\,A\}-0{\cdot}0000048v_{C'}-0{\cdot}000013v_{B}. \quad (17)$$

In the small term $0{\cdot}000013v_B$ it will be sufficient if we write $v_B = v_{C'}\,x_B/x_{C'}$.
Thus, for the original equation $Q = H-shv_{C'}$, p. 386, we must substitute

$$Q = 0{\cdot}2406A\,\{(1-0{\cdot}057A)\,P_0-(0{\cdot}021+0{\cdot}00011\tau)\,A\} \\ -\left(sh+0{\cdot}0000048+0{\cdot}000013\frac{x_B}{x_{C'}}\right)v_{C'}.$$

---

* For simplicity, the loss of heat along the wires of the upper temperature measuring sleeve, p. 392, is treated as if it took place from the heating sleeve.

Hence in the equation (4) for k (p. 386) we must write for H

$$0\cdot2406\mathrm{A}\{(1-0\cdot057\mathrm{A})\mathrm{P}_0-(0\cdot021+0\cdot00011\tau)\},$$

and for sh

$$sh+0\cdot0000048+0\cdot000013\frac{x_{\mathrm{B}}}{x_{\mathrm{C'}}}.$$

We thus obtain

$$kq\cosh\left(\frac{ph}{qk}\right)^{1/2}x_{\mathrm{C}}=\frac{0\cdot2406\mathrm{A}\{(1-0\cdot057\mathrm{A})\mathrm{P}_0-(0\cdot021+0\cdot00011\tau)\}}{v_{\mathrm{B}}-v_{\mathrm{A}}}(x_{\mathrm{B}}\mathrm{S}_{\mathrm{B}}-x_{\mathrm{A}}\mathrm{S}_{\mathrm{A}})$$
$$-\left(sh+0\cdot0000048+0\cdot000013\frac{x_{\mathrm{B}}}{x_{\mathrm{C'}}}\right)x_{\mathrm{C'}}\mathrm{S}_{\mathrm{C'}}.$$

Finally, substituting for the temperatures of the rod v_{B} and v_{A} in terms of $\bar{v}_{\mathrm{B}}$ and $\bar{v}_{\mathrm{A}}$ the observed mean temperatures of the platinum resistances by means of equation (12), p. 392, we have

$$kq\cosh\left(\frac{ph}{qk}\right)^{1/2}x_{\mathrm{C}}=\frac{0\cdot2406\mathrm{A}\{(1-0\cdot057\mathrm{A})\mathrm{P}_0-(0\cdot021+0\cdot00011\tau)\}}{(1\cdot026+29h)(\bar{v}_{\mathrm{B}}-\bar{v}_{\mathrm{A}})}(x_{\mathrm{B}}\mathrm{S}_{\mathrm{B}}-x_{\mathrm{A}}\mathrm{S}_{\mathrm{A}})$$
$$-\left(sh+0\cdot0000048+0\cdot000013\frac{x_{\mathrm{B}}}{x_{\mathrm{C'}}}\right)x_{\mathrm{C'}}\mathrm{S}_{\mathrm{C'}},$$

that is,

$$kq\cosh\left(\frac{ph}{qk}\right)^{1/2}x_{\mathrm{C}}$$
$$=\frac{(0\cdot2345-28h)\mathrm{A}\{(1-0\cdot057\mathrm{A})\mathrm{P}_0-(0\cdot021+0\cdot00011\tau)\}}{\bar{v}_{\mathrm{B}}-\bar{v}_{\mathrm{A}}}(x_{\mathrm{B}}\mathrm{S}_{\mathrm{B}}-x_{\mathrm{A}}\mathrm{S}_{\mathrm{A}})$$
$$-\left(sh+0\cdot0000048+0\cdot000013\frac{x_{\mathrm{B}}}{x_{\mathrm{C'}}}\right)x_{\mathrm{C'}}\mathrm{S}_{\mathrm{C'}},\qquad(18)$$

where $s=1\cdot47+0\cdot36+0\cdot11=1\cdot94$ sq. centims.

Effect of the use of the Variable State of Temperature Distribution.

So far the theory has been worked out on the assumption that the temperature distribution throughout the apparatus is steady. But it has been stated that the measurements were made during the gradual rise of temperature from that of liquid air. We have therefore to consider the effect of this on our fundamental equation (4).

Let v be the temperature of the bar at a cross section distant x from that where the bar joins the enclosing tube, and let V be the temperature of the tube. Then v satisfies the conditions

$$\left.\begin{aligned}qcp\frac{\partial v}{\partial t}&=qk\frac{\partial^2 v}{\partial x^2}-ph(v-\mathrm{V}),\\ \mathrm{V}&=f(t),\quad v=\mathrm{V}\text{ at }x=0,\\ qk\frac{\partial v}{\partial x}+ph(v-\mathrm{V})&=\mathrm{Q}\text{ at }x=x_{\mathrm{C}},\text{ the free end of the bar,}\end{aligned}\right\}$$

the heat Q being supposed imparted to the bar at its free end.

Let $v = v_0 + v_1$, where v_0 is independent of t, and $v_0 + v_1$ satisfy the following conditions,

$$\left.\begin{aligned} 0 &= qk\frac{\partial^2 v_0}{\partial x^2} - phv_0, \\ v_0 &= 0 \text{ at } x = 0, \\ qk\frac{\partial v_0}{\partial x} + phv_0 &= \mathrm{Q} \text{ at } x = x_{\mathrm{C}}, \end{aligned}\right\}$$

$$\left.\begin{aligned} qc\rho\frac{\partial v_1}{\partial t} &= qk\frac{\partial^2 v_1}{\partial x^2} - ph(v_1 - \mathrm{V}), \\ \mathrm{V} &= f(t), \quad v_1 = \mathrm{V} \text{ at } x = 0, \\ qk\frac{\partial v_1}{\partial x} + ph(v_1 - \mathrm{V}) &= 0 \text{ at } x = x_{\mathrm{C}}, \end{aligned}\right\}$$

then $v_0 + v_1$ obviously satisfies the conditions laid down for v. The solution of the equations for v_0 is

$$v_0 = \frac{\mathrm{Q}}{(phqk)^{1/2}} \sinh\left(\frac{ph}{qk}\right)^{1/2} x \Big/ \left[\cosh\left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}} + \left(\frac{ph}{qk}\right)^{1/2} \sinh\left(\frac{ph}{qk}\right)^{1/2} x_{\mathrm{C}}\right].$$

Hence $v_0 = 0$ when $\mathrm{Q} = 0$.

Since v_1 is independent of Q, we have at any instant for all values of x

$$v_1 \text{ with Q finite} - v_1 \text{ with Q zero} = v_0.$$

Since, however, v_1 cannot be observed at the same instant with Q zero and Q finite, temperatures are observed alternately with Q zero and Q finite, and the distribution with Q finite compared with the distribution with Q zero calculated for the same instant by interpolation between the observations with Q zero made immediately before and after.

In all but three or four cases it was only necessary to take the mean of the observations with Q zero taken before and after.

Since $f(t)$ is a continuous function the error committed by this method of observation will be very small.

Standardisation of Platinum Thermometers.

As the observations of conductivity were made over the range of temperature between about −180° C. and 30° C., the temperatures selected for standardising the thermometers used were the boiling point of liquid oxygen, the freezing point and the boiling point of water.

The two thermometers were slipped on to a short rod of brass 2 centims. in length and of the same diameter as the rods used throughout the work. The rod and thermometers were then placed in a short brass tube about 3 centims. long, one end of which was closed by a brass plate. Through a cork in the other end of it the thermometer leads and a pair of compensating leads similar to those of the thermometers passed to a series of mercury cups, which allowed either of the thermometers or the compensating leads to be connected to a resistance box.

The coils of this box were of platinum silver wire, and were multiples of the B.A. ohm at 15°·5 C. The fixed arms of the resistance bridge were the 10- and 1000-ohm coils of the box respectively, and any error in the ratio of these two was eliminated by substituting a 1- or 2-ohm standard resistance coil for the thermometers and finding its apparent resistance. This enables the box readings to be converted to true ohms.

The following is a record of one of the tests.

Hartmann and Braun 2-ohm standard correct at 17°·3 C. Temperature coefficient 0·0002. Temperature of room, 15°·5 C. Hence standard = 1·9993 ohm.

Standard+leads = 2·0477 apparent ohms of box.
Leads = 0·0266 ,, ohm ,,
Standard 1·9993 ohms = 2·0211 ,, ohms ,,

Other tests agreed to within one part in 5000.

The resistances recorded in what follows have all been reduced to standard ohms.

The current used in the bridge was derived from a pint Leclanché cell connected to the bridge through a resistance of 53 ohms.

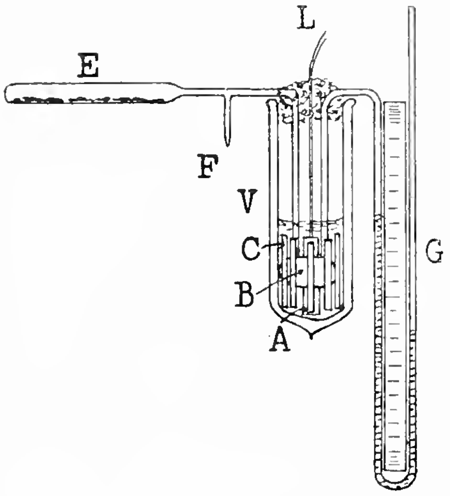

Fig. 2.

The test of the resistances of the measuring coils at the low temperature was made with the arrangement shown in fig. 2.

A is the short brass cylinder containing the measuring coils, the leads L of which, and the compensating leads, pass through a cork closing the top of the cylinder. B is the bulb of the oxygen vapour-pressure thermometer* EFG used to determine the temperature on the constant-volume hydrogen scale of the liquid air in the Dewar vessel V.

C represents six short copper rods placed round A and B to keep the temperature of the liquid air uniform. E is a bulb containing crystals of potassium permanganate which on heating furnish the oxygen. F is the sealed tube through which the thermometer was exhausted before use. G is the mercury gauge to determine the vapour pressure of the oxygen condensed in the bulb B.

The difference of level of the mercury in G was initially 76·73 centims., and the height of the barometer 76·77 centims.

Liquid air having been poured into the Dewar tube V till it was almost full, and the opening of the tube plugged with cotton wool, the bulb E was heated so as to generate the oxygen, which condensed in B. The vapour pressure indicated initially

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* I adopted this method of standardisation on the suggestion of Dr. M. W. TRAVERS, F.R.S., and found it most convenient.

was 31·32 centims., corresponding, according to TRAVERS' determinations, to 82°·4 C. absolute, and rose during the first 40 minutes to 33·61 centims., corresponding to a temperature of 82°·9 C. During the next 16 minutes the following measurements were taken :—

Elliott B.A. box, ratio arms 10 : 1000.

h.	m.		
11	52	manometer	43·16 centims.
11	54	compensating leads .	0·0964 ohm (apparent).
11	56	lower coil	0·8285 ,, ,,
11	58	upper ,, ...	0·8332 ,, ,,
12	0	manometer	42·77 centims.
12	2	upper coil	0·8335 ohm (apparent).
12	4	lower ,, ...	0·8295 ,, ,,
12	6	compensating leads .	0·0967 ,, ,,
12	8	manometer	42·51 centims.

Barometer 76·79 centims., temperature 15°·5 C.

From these observations we deduce that, at a mean pressure of 33·99 centims. of mercury at 15°·5 C., or 33·92 centims. of mercury at 0° C., at sea-level in latitude 45°, under which oxygen boils at 82°·9 C. absolute on the constant volume hydrogen thermometer, the resistances of the coils were :—

Upper coil . . 0·8333−0·0966 = 0·7367 apparent ohm = 0·7286 true ohm.
Lower ,, . . 0·8290−0·0966 = 0·7324 ,, ,, = 0·7243 ,, ,,

The determinations of resistance at the freezing point of water were made by placing the brass tube containing the coils at a depth of about 5 centims. in clean ice shavings contained in a brass can with holes in the bottom to allow the ice to drain. After the apparatus had stood for half an hour the following observations were made :—

h.	m.		
1	0	compensating leads . .	0·1152 ohm (apparent).
1	2	lower coil	2·877 ohms ,,
1	4	upper ,, ...	2·882 ,, ,,
1	6	,, ,, ...	2·882 ,, ,,
1	8	lower ,, ...	2·877 ,, ,,
1	10	compensating leads . .	0·1153 ohm ,,

From these observations we deduce that the resistances of the coils at the melting point of ice were :—

Upper coil . . 2·882−0·115 = 2·767 apparent ohms = 2·736 true ohms.
Lower ,, . . 2·877−0·115 = 2·762 ,, ,, = 2·731 ,, ,,

In the resistance determinations at the boiling point of water the coils with the brass rod through them were placed in a narrow brass tube 12 centims. long, the top closed by a cork through which the leads passed, and the whole placed in a hypsometer with the lower 11 centims. of the tube exposed to the steam. Owing to the uncertain behaviour of the shellac on which the insulation of the coils depended in the presence of moisture at this temperature, the coils were well dried by being kept at 100° C. for about an hour and a half before the following measurements were taken :—

h.	m.				
3	40	compensating leads . .	0·1223	ohm	(apparent).
3	42	lower coil	3·874	ohms	,,
3	44	upper ,, ...	3·878	,,	,,
3	46	,, ,, ...	3·878	,,	,,
3	48	lower ,, ...	3·876	,,	,,
3	50	compensating leads . .	0·1219	ohm	,,

Barometer 76·78 centims. at 15°·5 C. = 76·63 centims. at 0° C. at sea-level in latitude 45°.

From these measurements we conclude that the resistances of the coils at a temperature of 100°·23 C. are :—

Upper coil . . 3·878 − 0·122 = 3·756 apparent ohms = 3·715 true ohms.
Lower ,, . . 3·875 − 0·122 = 3·753 ,, ,, = 3·712 ,, ,,

Although the slight excess of the resistance of the upper coil over that of the lower coil is not proportional to that of either coil, it is so small in amount that it will be sufficient in defining the platinum temperature scale for the coils used and in reducing it to the standard hydrogen scale to use the means of the observed resistances at each temperature.

We thus have for the platinum temperature t_P corresponding to a resistance R of either coil

$$t_P = \frac{R-2\cdot734}{0\cdot980}\,100^\circ\cdot23 = 102\cdot3\,(R-2\cdot734), \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

and as the basis of the connection between the platinum and hydrogen scales the following :—

Temperature t_H on hydrogen scale.	Resistance.
82°·9 C. absolute = −190°·1 C.	0·726 ohm.
273°·0 C.* ,, = 0° C.	2·734 ohms.
373°·23 C. ,, = 100°·23 C.	3·714 ,,

In order to compare the platinum used with that used by other experimenters, the "fundamental constants" of CALLENDAR are calculated as follows :—

$$\text{“Fundamental coefficient”} = \frac{3\cdot714-2\cdot734}{2\cdot734\times100\cdot23} = \frac{0\cdot980}{274\cdot0} = 0\cdot00358.$$

$$\text{“Fundamental zero”} = -\frac{1}{0\cdot00358} = -279^\circ\cdot3.$$

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* CHAPPUIS, 'Travaux et Mémoires du Bureau International,' VI., p. 108.

The temperature on the platinum thermometer corresponding to $-190^\circ{\cdot}1$ C. or $82^\circ{\cdot}9$ C. absolute on the hydrogen thermometer is

$$\frac{0{\cdot}726-2{\cdot}734}{2{\cdot}734\times 0{\cdot}00358} = -205^\circ{\cdot}2.$$

The δ of the difference equation

$$t_{\text{H}}-t_{\text{P}} = \delta\left(\frac{t_{\text{H}}}{100}-1\right)\frac{t_{\text{H}}}{100} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

is then given by

$$15{\cdot}1 = \delta\left(-\frac{190}{100}-1\right)\left(-\frac{190}{100}\right), \quad \text{or} \quad \delta = \frac{15{\cdot}1}{5{\cdot}51} = 2{\cdot}74.$$

The platinum wire is, therefore, nearly identical in properties with that used as a standard by Dewar and Fleming,* the fundamental constants of which Callendar has calculated,† and appears to be rather less pure than that used by me in the determination of the heat conductivities of some substances which are electrical insulators at low temperatures.‡

The connection between the two temperature scales (20), and between the conductivities according to the two scales,

$$k_{\text{H}} = k_{\text{P}}\frac{dt_{\text{P}}}{dt_{\text{H}}}, \ i.e., \ k_{\text{H}} = k_{\text{P}}\left\{1+\delta\left(0{\cdot}01-t_{\text{H}}/50{,}000\right)\right\}, \quad . \quad . \quad . \quad . \qquad (21)$$

is shown in the following table§:—

Table of Connection between Temperatures and Thermal Conductivities on the Platinum Scale used and the Hydrogen Scale.

t_{H}.	t_{P}.	$k_{\text{H}}/k_{\text{P}}$.	t_{H}.	t_{P}.	$k_{\text{H}}/k_{\text{P}}$.
°	°		°	°	
100	100	0·973	− 60	− 62·6	1·060
90	90·2	0·978	− 70	− 73·3	1·066
80	80·4	0·984	− 80	− 84·0	1·071
70	70·6	0·989	− 90	− 94·7	1·077
60	60·7	0·995	− 100	− 105·5	1·082
50	50·7	1·000	− 110	− 116·3	1·088
40	40·7	1·006	− 120	− 127·2	1·093
30	30·6	1·011	− 130	− 138·2	1·099
20	20·4	1·016	− 140	− 149·2	1·104
10	10·2	1·022	− 150	− 160·3	1·110
0	0	1·027	− 160	− 171·4	1·115
− 10	− 10·3	1·033	− 170	− 182·6	1·121
− 20	− 20·7	1·038	− 180	− 193·8	1·126
− 30	− 31·1	1·044	− 190	− 205·1	1·132
− 40	− 41·5	1·049	− 200	− 216·4	1·137
− 50	− 52·1	1·056			

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* 'Phil. Mag.,' 40, p. 100 (1895).

† 'Phil. Mag.,' 47, p. 213 (1899).

‡ 'Phil. Trans.,' A, 204, p. 451 (1905).

§ Compare Callendar, 'Phil. Mag.,' 47, p. 214 (1899).

Standardisation of Resistance Bridge.

The standardisation of the resistance bridge used in determining the resistances of the temperature coils during a conductivity experiment was effected by substituting standard coils of 0·1, 0·2, 0·5, 1·0, and 2·0 ohms for one of the temperature coils, and adjusting the bridge to a balance as in the experiments.

The standardisation of each of the resistances of the dial used in the measurement of the difference of the resistances of the two platinum coils, from which the difference of temperature of the two points x_A and x_B of the test bar is calculated, was effected by substituting for it a standard coil of 0·01006 ohm by Hartmann and Braun, and examining the effect of the substitution on the balance of the bridge.

The resistance, 0·1055 ohm, found by adding together the resistances of the ten coils found in this way, agrees very well with the value 0·1057 found by direct comparison of the dial with a Wolff 0·1-ohm standard after the experiments were completed.

In the tables of observations which follow, the values of the resistances given are the corrected ones.

Standardisation of Ammeter and Voltmeter.

The Weston milliamperemeter No. 5491, which was used throughout the work to measure the current through the coil in which the heat was generated, was standardised by comparison with a Kelvin balance which had been checked by the copper voltmeter. It was found to read 1 per cent. too high. The values of the current given in the following tables are the corrected values.

The Keiser and Schmidt moving-coil voltmeter was compared by a potentiometer method with a cadmium and a Clark cell, either separately, in series, or in opposition. The electromotive force of each cell had been determined by comparison with a standard Clark. It was found to read 0·8 per cent. too high. The values given in the following tables are corrected values.

Determination of the Coefficient "h" of Loss of Heat from the Surface of the Rod.

The final expression for the thermal conductivity k of the material of the rods, equation (18), p. 396, involves a knowledge of h, the heat lost in 1 second from 1 sq. centim. of surface of the bar when that area is 1° C. hotter than the surrounding tube. As the terms involving h only affect the result to a small extent, an approximate value of the quantity is sufficient.

To determine this value, the heating coil and upper temperature measuring coil were placed on a brass rod 5·2 centims. long, so as to divide the rod into three equal parts. This rod with its coils was suspended in the centre of the tube. A short brass rod 2 centims. long was fitted into the base of the tube, and on the end projecting into the tube the lower temperature measuring coil was placed. The coils were connected up as in an experiment to determine conductivity.

On sending a small current through the heating coil the temperature of the rod in the centre is raised, and when equilibrium between the electrical supply of heat and the loss of heat from the surface of the rod had been attained, the excess of temperature of the rod over the temperature of the shorter one continuous with the enclosing tube was observed. The temperature of the latter and the supply of power to the central rod were also measured. To get rid of the effect of the slow change of temperature of the enclosure the heating current was then switched from the rod to the enclosure, and the difference of temperature between rod and enclosure again measured after the steady state had been attained.

The same series of observations was made at about 100°, 200° and 300° absolute temperature.

The total quantity of heat, H, imparted to the bar per second by the heating coil is given in gram-degrees by equation (17), p. 395, as

$$\mathrm{H} = 0{\cdot}2406\mathrm{A}\ \{(1-0{\cdot}057\mathrm{A})\,\mathrm{P}_0-(0{\cdot}021+0{\cdot}00011\tau)\,\mathrm{A}\}-0{\cdot}0000048v_{\mathrm{C}'}-0{\cdot}000013v_{\mathrm{B}},$$

where A = amperes sent through coil,

P_0 = volts at ends of leads,

τ = absolute temperature of enclosure.

$v_{\mathrm{C}'} = v_{\mathrm{B}}$ = excess of temperature of rod over that of enclosure.

If S is the total surface of rod and sleeves, and the coefficient h of loss from surfaces of rod and sleeve be assumed to be the same, since both were slightly oiled surfaces, we have

$$\mathrm{H} = \mathrm{S}hv_{\mathrm{B}}.$$

Hence

$$h\mathrm{S} = 0{\cdot}2406\mathrm{A}\ \{(1-0{\cdot}057\mathrm{A})\,\mathrm{P}_0-(0{\cdot}021+0{\cdot}00011\tau)\,\mathrm{A}\}\ v_{\mathrm{B}}^{-1}-0{\cdot}000018.$$

Now

$\mathrm{S} = 2\ \{(2{\cdot}28\times0{\cdot}42)+(2{\cdot}14\times0{\cdot}31)\}$ for sides and ends of sleeves,

$+(5{\cdot}2-1{\cdot}3)\ 1{\cdot}84+(2\times0{\cdot}27)$,, ,, ,, rod,

$= 10{\cdot}96$ sq. centims.

$v_{\mathrm{B}} = (1{\cdot}026+28{\cdot}6h)\ \bar{v}_{\mathrm{B}}$ (12), p. 392, and $\bar{v}_{\mathrm{B}} = 102{\cdot}3\ (\mathrm{R}_{\mathrm{B}}-\mathrm{R}_{\tau})$ (19), p. 400.

where $\bar{v}_{\mathrm{B}}$ is the mean temperature of the platinum temperature coil on the rod, R_{B} its resistance, R_{τ} that of the coil in thermal contact with the enclosure.

Thus

$$h = \frac{1}{10{\cdot}96}\left\{\frac{0{\cdot}2406\mathrm{A}\,[(1-0{\cdot}057\mathrm{A})\,\mathrm{P}_0-(0{\cdot}021+0{\cdot}00011\tau)\,\mathrm{A}]}{(1{\cdot}026+29h)\,102{\cdot}35\,(\mathrm{R}_\mathrm{B}-\mathrm{R}_\tau)}-0{\cdot}000018\right\},$$

i.e.,

$$h = 0{\cdot}000214\mathrm{A}\,\frac{(1-0{\cdot}057\mathrm{A})\,\mathrm{P}_0-(0{\cdot}021+0{\cdot}00011\tau)\,\mathrm{A}}{(1{\cdot}026+29h)\,(\mathrm{R}_\mathrm{B}-\mathrm{R}_\tau)}-0{\cdot}0000016. \quad . \quad (22)$$

The table on p. 405 gives the observations and their reduction.

Although the determination of the general law of variation of the coefficient h with temperature is not necessary for the purpose of the present work, it may be of interest to point out that the observed values of h for the three values of the mean temperature of rod and enclosure measured on the hydrogen temperature scale do not agree with any of the formulæ which have been proposed to express that variation. LORENZ[*] proposed the formula $h \propto 1+bt^{1/4}$, but WAGNER[†] has recently found it unsuitable and suggests $h \propto 1+bt^2$, while I found[‡] $h \propto t^n$, where $n = 0{\cdot}26$, suitable over a comparatively small range of temperature. The present observations suggest the expression $h \propto 1+bt^{3/2}$ for the case of a small rod at very low temperatures in an enclosure only a few, say 10, degrees cooler than itself. t is the mean temperature of rod and enclosure on the hydrogen thermometer scale.

Results of Thermal Conductivity Experiments.

In the Tables of Observations and Results which follow, the values of the quantities observed are given after correction for errors, if any, of the observing instruments. In addition, a few of the most important quantities involved in the calculation of the conductivities are given, in order to facilitate comparison of the different experiments with each other, and to enable errors in the calculations to be more readily detected.

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[*] L. LORENZ, 'Ann. der Physik,' 13, p. 582 (1881).

[†] R. WAGNER, 'Beiblätter,' 27, p. 534 (1903).

[‡] C. H. LEES, 'Phil. Mag.,' 28, p. 429 (1889).

TABLE of Observations for h.

τ, abs. Pt. scale.	A.	P_0.	$(1-0\cdot057\,A)\times P_0$.	$(0\cdot021+0\cdot00011\tau)\,A$.	$(1-0\cdot057A)\,P_0-(0\cdot021+0\cdot00011\tau)\,A$.	$A\,\{(1-0\cdot057A)\,P_0-(0\cdot021+0\cdot00011\tau)\,A\}$.	Difference of resistance of two coils observed.	R_B-R_τ.	$1\cdot026+29h$.	$(R_B-R_\tau)\times(1\cdot026+29h)$.	$A\,\dfrac{(1-0\cdot057A)\,P_0-(0\cdot021+0\cdot00011\tau)\,A}{(1\cdot026+29h)\,(R_B-R_\tau)}$.	$0\cdot000214A\,\dfrac{(1-0\cdot057A)\,P_0-(0\cdot021+0\cdot00011\tau)\,A}{(1\cdot026+29h)\,(R_B-R_\tau)}$.	h.	Mean absolute platinum temperature of rod and enclosure.	Mean temperature of rod and enclosure on hydrogen scale.
° C.	amp.	volt					ohm	ohm						° C.	° C.
298	·120	·720	·715	·006	·709	·0851	·0915	·0873	1·032	·0901	·945	·000202	·000200	302·5	+ 23
298	0						·0042								
228	0						− ·0437								
206	·123	·723	·718	·005	·713	·0877	·0698	·1123	1·031	·1158	·758	·000162	·000160	212·0	− 64
206	0						− ·0425	calculated							
106	·122	·696	·691	·004	·687	·0838	·0987	·1357	1·030	·1398	·599	·000128	·000126	113·0	− 155
106	0						− ·0370	calculated							
96	0						− ·0365								

COPPER ROD.

Turned from a Length of Soft-drawn High-conductivity Copper Conductor. Density* at 23° C. = 8·84.

$a_2 = 3·65$ centims., approx. $k = ·9$, therefore $b' = ·32$, $x_A = ·42$, $x_B = 4·71$, $x_C = 5·13$, $x_{C'} = 5·35$ centims., $s = 1·83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	$\frac{\text{Heat}}{\text{temp. difference.}}$	$\sqrt{6·85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.†	II.†	III.†	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 27	·340	2·084	·688	·157	·0310	·0268	2·74	·0572	·039	4·31	·247	·245	·273	·898	+ 26	·910
+ 25	0				·0042											
− 189	0				− ·0017											
− 179	·348	2·020	·685	·158	·0229	·0246	2·52	·0627	·031	4·31	·269	·267	·271	·985	− 166	1·105
− 176	0				− ·0017											
− 166	·347	2·022	·684	·158	·0243	·0256	2·62	·0603	·031	4·31	·260	·258	·271	·952	− 154	1·061
− 157	0				− ·0010											
− 147	·347	2·030	·686	·158	·0252	·0260	2·66	·0593	·032	4·31	·256	·254	·271	·937	− 137	1·036
− 144	0				− ·0007											
− 136	·347	2·032	·686	·158	·0260	·0269	2·75	·0573	·032	4·31	·247	·245	·271	·905	− 127	·996
− 133	0				− ·0010											
− 125	·346	2·036	·685	·158	·0261	·0269	2·75	·0573	·033	4·31	·247	·245	·272	·901	− 118	·989
− 122	0				− ·0008											
− 116	·346	2·040	·687	·158	·0261	·0269	2·75	·0573	·034	4·31	·247	·245	·272	·901	− 109	·982
− 113	0				− ·0011											
− 98	·346	2·044	·688	·158	·0261	·0269	2·75	·0573	·034	4·31	·247	·245	·272	·901	− 93	·974
− 96	0				− ·0008											
− 87	·346	2·050	·690	·159	·0267	·0272	2·78	·0571	·034	4·31	·246	·244	·272	·898	− 83	·965
− 83	0				− ·0003											
− 73	·345	2·060	·691	·159	·0271	·0273	2·79	·0569	·035	4·31	·245	·243	·272	·894	− 70	·955
− 71	0				− ·0002											
− 62	·345	2·060	·691	·158	·0272	·0272	2·78	·0567	·035	4·31	·245	·243	·272	·894	− 60	·950
− 56	0				·0002											
− 47	·344	2·064	·691	·158	·0278	·0273	2·79	·0569	·036	4·31	·245	·243	·272	·894	− 45	·941
− 44	0				·0006											
− 39	0				·0002											

− 31 − 24	·346 0	2·100	·707	·162	·0281 ·0008	·0276	2·82	·0573	·037	4·31	·247	·245	·273	·898	− 30	·939
− 15 − 11	·346 0	2·110	·710	·163	·0288 ·0012	·0278	2·85	·0571	·037	4·31	·246	·244	·273	·894	− 15	·927
− 4 0	·346 0	2·110	·710	·163	·0296 ·0021	·0280	2·87	·0567	·038	4·31	·245	·243	·273	·891	− 4	·918
+ 7 9	·345 0	2·114	·709	·163	·0298 ·0026	·0275	2·81	·0579	·038	4·31	·250	·248	·273	·909	+ 7	·932
16 19	·345 0	2·120	·711	·162	·0303 ·0028	·0276	2·82	·0573	·039	4·31	·247	·245	·273	·898	16	·915
25 27	·345 0	2·120	711	·162	·0305 ·0032	·0275	2·81	·0575	·039	4·31	·248	·246	·273	·902	25	·915

Duration of experiment, 6 hours.

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* For the determinations of density throughout I have to thank one of my senior students at the East London College, Miss F. VERINDER, B.Sc.

† Column I. $= \dfrac{\text{Heat supplied to rod per second}}{\text{Temperature difference}} (x_B S_B - x_A S_A)$.

Column II. $=$ Column I. $- \left(sh + \cdot 0000048 + \cdot 00001 \dfrac{x_B}{x_{C'}} \right) x_{C'} S_{C'}$.

Column III. $= q \cosh \left(\dfrac{ph}{qk} \right)^{1/2} x_C$.

SILVER ROD.

Turned from a Rod of Fine Silver ·999, supplied by Messrs. JOHNSON & MATTHEY. Density at 21° = 10·47.

$a_2 = 4\cdot35$ centims., approx $k = 1\cdot0$, therefore $b' = \cdot32$, $x_A = \cdot42$, $x_B = 5\cdot41$, $x_C = 5\cdot83$, $x_{C'} = 6\cdot05$ centims., $s = 1\cdot83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat temp. difference.	$\sqrt{6\cdot85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 28	0				+ ·0034											
33	·352	2·180	·744	·169	·0348	·0315	3·22	·0526	·037	5·03	·264	·261	·275	·951	+ 33	·961
31	0				·0033											
− 192	0				·0022											
− 176	·366	2·124	·757	·175	·0387	·0353	3·61	·0485	·029	5·01	·243	·241	·272	·885	− 163	·992
− 174	0				·0046											
− 169	0				·0001											
− 159	·366	2·140	·764	·175	·0351	·0347	3·55	·0493	·030	5·01	·248	·246	·272	·904	− 148	1·005
− 154	0				·0009											
− 142	·366	2·150	·767	·176	·0356	·0346	3·54	·0497	·030	5·01	·250	·248	·272	·910	− 133	1·006
− 139	0				·0012											
− 132	·365	2·141	·765	·176	·0358	·0345	3·53	·0499	·031	5·02	·251	·249	·272	·914	− 124	1·004
− 130	0				·0015											
− 120	·365	2·160	·769	·177	·0359	·0343	3·51	·0505	·031	5·02	·254	·252	·272	·925	− 113	1·011
− 119	0				·0018											
− 114	0				·0016											
− 105	·363	2·170	·768	·177	·0354	·0342	3·50	·0506	·032	5·02	·255	·253	·273	·925	− 99	1·003
− 103	0				·0009											
− 90	·361	2·170	·760	·174	·0334	·0331	3·39	·0514	·033	5·02	·258	·256	·273	·940	− 86	1·013
− 85	0				− ·0002											
− 72	·366	2·210	·786	·180	·0342	·0344	3·52	·0512	·033	5·02	·257	·255	·273	·936	− 69	1·000
− 69	0				− ·0002											
− 55	·368	2·230	·797	·182	·0343	·0345	3·53	·0516	·034	5·02	·259	·257	·273	·943	− 53	·999
− 50	0				− ·0002											
− 39	·368	2·230	·797	·182	·0344	·0344	3·52	·0517	·034	5·02	·259	·257	·273	·943	− 38	·991
− 35	0				·0002											
− 22	·368	2·240	·801	·183	·0347	·0343	3·51	·0522	·035	5·02	·262	·260	·273	·954	− 21	·993
− 21	0				·0006											
− 12	·367	2·250	·802	·183	·0354	·0342	3·50	·0523	·036	5·02	·262	·260	·274	·951	− 12	·985
− 7	0				·0018											
+ 1	·368	2·250	·805	·184	·0358	·0338	3·46	·0532	·036	5·02	·267	·265	·274	·969	+ 1	·996
2	0				·0021											
10	·366	2·254	·802	·183	·0360	·0337	3·45	·0531	·037	5·03	·267	·265	·275	·965	10	·989
11	0				·0024											
18	·367	2·260	·806	·183	·0366	·0341	3·49	·0525	·037	5·03	·264	·262	·275	·955	18	·973
20	0				·0027											
27	·367	2·260	·806	·183	·0369	·0341	3·49	·0525	·037	5·03	·264	·261	·275	·951	27	·964
26	0				·0029											
32	·366	2·264	·805	·183	·0370	·0339	3·47	·0528	·037	5·03	·265	·262	·275	·955	32	·965
31	0				·0032											

Duration of experiment, 5 hours 10 minutes.

ZINC ROD.

Turned from a Cast Stick of "Pure redistilled Zinc." Fracture crystalline, with Crystals radiating from Axis of Rod. Density at 21° C. = 7·10.

$a_2 = 4\cdot10$ centims., approx. $k = \cdot26$, therefore $b' = \cdot29$, $x_A = \cdot39$, $x_B = 5\cdot07$, $x_C = 5\cdot46$, $x_{C'} = 5\cdot65$ centims. $s = 1\cdot83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat / temp. difference.	$\sqrt{6\cdot85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 21	0				+ ·0032											
24	·205	1·236	·248	·0565	·0375	·0342	3·50	·0161	·073	4·80	·0773	·0749	·290	·258	+ 24	·262
22	0				·0032											
− 199	0				− ·0027											
− 188	·211	1·200	·249	·0575	·0354	·0372	3·81	·0151	·057	4·75	·0718	·0704	·281	·251	− 174	·283
− 184	0				− ·0009											
− 174	·212	1·210	·252	·0582	·0370	·0374	3·83	·0152	·057	4·75	·0723	·0708	·281	·252	− 161	·283
− 174	0				·0000											
− 163	·212	1·215	·253	·0582	·0359	·0373	3·82	·0152	·058	4·75	·0722	·0707	·282	·251	− 150	·280
− 162	0				− ·0020											
− 155	·212	1·220	·254	·0584	·0359	·0379	3·88	·0150	·059	4·76	·0715	·0699	·282	·248	− 144	·275
− 152	0				− ·0020											
− 144	·212	1·230	·256	·0589	·0363	·0382	3·91	·0150	·060	4·76	·0715	·0699	·283	·247	− 134	·273
− 141	0				− ·0019											
− 133	·212	1·230	·256	·0589	·0368	·0384	3·93	·0149	·061	4·76	·0710	·0693	·283	·245	− 124	·270
− 132	0				− ·0014											
− 123	·212	1·231	·256	·0589	·0366	·0384	3·93	·0149	·062	4·76	·0710	·0693	·284	·244	− 115	·267
− 122	0				− ·0023											
− 113	·212	1·235	·257	·0591	·0353	·0388	3·97	·0149	·062	4·76	·0710	·0693	·284	·244	− 107	·266
− 111	0				− ·0028											
− 101	0				− ·0055											
− 91	·208	1·225	·249	·0573	·0313	·0365	3·74	·0153	·063	4·77	·0730	·0712	·284	·251	− 87	·271
− 84	0				− ·0048											
− 73	·207	1·230	·250	·0575	·0313	·0359	3·67	·0157	·065	4·77	·0749	·0730	·285	·256	− 69	·274
− 70	0				− ·0044											
− 61	·207	1·230	·250	·0572	·0313	·0357	3·65	·0157	·066	4·77	·0749	·0730	·286	·255	− 59	·271
− 54	0				− ·0042											
− 40	·207	1·230	·250	·0572	·0317	·0354	3·62	·0158	·068	4·78	·0756	·0736	·287	·256	− 39	·269
− 35	0				− ·0032											
− 23	·207	1·235	·251	·0575	·0321	·0349	3·57	·0161	·069	4·79	·0772	·0750	·288	·261	− 22	·272
− 18	0				− ·0025											
− 9	·206	1·240	·250	·0572	·0326	·0345	3·53	·0162	·070	4·79	·0777	·0755	·288	·262	− 9	·271
− 5	0				− ·0012											
+ 4	·206	1·240	·250	·0572	·0342	·0348	3·56	·0161	·071	4·79	·0772	·0749	·289	·259	+ 4	·266
7	0				·0000											
15	·206	1·242	·250	·0570	·0347	·0343	3·51	·0162	·072	4·80	·0778	·0755	·289	·261	15	·267
16	0				·0009											
23	·206	1·245	·251	·0572	·0355	·0343	3·51	·0163	·073	4·80	·0783	·0759	·290	·262	23	·266
23	0				·0015											

Duration of experiment, 6·hours 20 minutes.

* See note on p. 407.

ZINC ROD (Second Experiment).

$a_2 = 2{\cdot}32$ centims., approx. $k = {\cdot}26$, therefore $b' = {\cdot}29$, $x_A = {\cdot}39$, $x_B = 3{\cdot}29$, $x_C = 3{\cdot}68$, $x_{C'} = 3{\cdot}87$ centims.; $s = 1{\cdot}83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	$\frac{\text{Heat}}{\text{temp. difference.}}$	$\sqrt{6{\cdot}85\frac{h}{k}}$	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 19	0				+ ·0032											
24	·270	1·640	·433	·0987	·0413	·0381	3·90	·0253	·073	2·93	·0741	·0725	·278	·261	+ 24	·265
21	0				·0032											
− 195	0				− ·0044											
− 182	·279	1·610	·439	·1014	·0384	·0427	4·37	·0232	·057	2·92	·0678	·0668	·274	·244	− 169	·275
− 179	0				− ·0042											
− 167	·280	1·626	·446	·1024	·0395	·0435	4·45	·0231	·058	2·92	·0675	·0665	·274	·243	− 155	·272
− 164	0				− ·0037											
− 153	·282	1·640	·453	·1042	·0404	·0439	4·49	·0232	·059	2·92	·0678	·0667	·275	·247	− 142	·275
− 152	0				− ·0034											
− 141	·282	1·650	·455	·1047	·0412	·0444	4·54	·0230	·060	2·92	·0672	·0661	·275	·240	− 132	·265
− 141	0				− ·0029											
− 131	·282	1·660	·458	·1054	·0415	·0442	4·52	·0233	·061	2·92	·0681	·0670	·275	·244	− 123	·269
− 129	0				− ·0025											
− 121	·282	1·660	·458	·1054	·0419	·0442	4·52	·0233	·062	2·92	·0681	·0670	·275	·244	− 114	·267
− 121	0				− ·0020											
− 114	0				− ·0031											
− 102	·285	1·700	·475	·1093	·0419	·0447	4·58	·0238	·063	2·92	·0696	·0684	·275	·249	− 97	·271
− 98	0				− ·0025											
− 87	·280	1·680	·461	·1060	·0412	·0434	4·44	·0238	·063	2·92	·0696	·0684	·275	·249	− 83	·268
− 84	0				− ·0019											
− 68	·284	1·710	·475	·1088	·0424	·0440	4·50	·0241	·065	2·92	·0704	·0691	·276	·250	− 65	·267
− 65	0				− ·0013											
− 51	·282	1·710	·472	·1081	·0423	·0437	4·47	·0241	·067	2·93	·0707	·0694	·276	·251	− 49	·265
− 46	0				− ·0014											
− 34	·282	1·710	·472	·1081	·0424	·0431	4·41	·0245	·068	2·93	·0718	·0704	·276	·255	− 33	·267
− 31	0				0000											
− 20	·283	1·730	·479	·1097	·0427	·0427	4·37	·0251	·069	2·93	·0735	·0720	·276	·261	− 19	·272
− 18	0				0000											
− 7	·283	1·734	·480	·1099	·0427	·0426	4·36	·0252	·070	2·93	·0738	·0723	·277	·261	− 7	·270
− 6	0				·0002											
+ 4	·283	1·740	·483	·1106	·0433	·0424	4·34	·0255	·071	2·93	·0747	·0732	·277	·265	+ 4	·272
4	0				·0019											
11	·282	1·740	·481	·1100	·0436	·0418	4·28	·0257	·072	2·93	·0753	·0738	·277	·267	11	·273
12	0				·0017											
20	·282	1·740	·481	·1097	·0437	·0418	4·28	·0256	·073	2·93	·0750	·0734	·278	·264	20	·269
20	0				·0021											
27	·282	1·744	·481	·1097	·0440	·0418	4·28	·0256	·073	2·93	·0750	·0734	·278	·264	27	·268
26	0				·0023											

Duration of experiment, 4 hours.

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* See note on p. 407.

Turned from a Cast Stick of "Pure Redistilled Cadmium" as used in Cadmium Cell. Density at 21° C. = 8·64.

$a_2 = 4{\cdot}32$ centims., approx. $k = {\cdot}217$, therefore $b' = {\cdot}29$, $x_A = {\cdot}39$, $x_B = 5{\cdot}29$, $x_C = 5{\cdot}68$, $x_{C'} = 5{\cdot}87$ centims.,
$s = 1{\cdot}83$ sq. centims.

Mean Pt. temp. of rod. ° C.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$ ohms.	Differences, ohms.	Pt. temp. differences.	Heat / temp difference.	$\sqrt{6{\cdot}85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod. ° C.	k_H.
+ 20	0				+ ·0029											
24	·219	1·330	·286	·0651	·0520	·0493	5·05	·0129	·079	5·06	·0655	·0630	·296	·213	+ 24	·216
21	0				·0026											
− 203	0				− ·0015											
− 191	·222	1·270	·277	·0639	·0486	·0513	5·25	·0121	·062	5·00	·0607	·0592	·285	·208	− 177	·235
− 177	0				− ·0039											
− 165	·219	1·264	·272	·0625	·0454	·0486	4·97	·0125	·063	5·00	·0627	·0611	·286	·213	− 153	·238
− 161	0				− ·0025											
− 150	·219	1·262	·272	·0625	·0461	·0481	4·92	·0127	·065	5·00	·0637	·0621	·287	·216	− 140	·239
− 147	0				− ·0015											
− 138	·220	1·270	·274	·0629	·0470	·0483	4·94	·0127	·066	5·01	·0638	·0620	·287	·216	− 129	·238
− 135	0				− ·0012											
− 126	·219	1·272	·274	·0629	·0476	·0486	4·97	·0126	·067	5·01	·0633	·0615	·288	·213	− 118	·234
− 125	0				− ·0008											
− 116	·218	1·272	·273	·0627	·0475	·0486	4·97	·0126	·068	5·02	·0635	·0617	·289	·213	− 109	·233
− 115	0				− ·0013											
− 105	·218	1·280	·274	·0629	·0462	·0484	4·95	·0127	·069	5·02	·0640	·0622	·289	·215	− 99	·234
− 101	0				− ·0031											
− 90	·218	1·279	·274	·0629	·0455	·0485	4·96	·0126	·070	5·02	·0635	·0616	·290	·212	− 86	·229
− 86	0				− ·0030											
− 76	0				− ·0052											
− 63	·217	1·290	·275	·0629	·0433	·0480	4·91	·0128	·072	5·03	·0646	·0626	·291	·215	− 60	·229
− 55	0				− ·0042											
− 43	·215	1·279	·270	·0617	·0434	·0472	4·83	·0127	·073	5·04	·0642	·0631	·291	·216	− 41	·227
− 36	0				− ·0034											
− 25	·214	1·280	·269	·0615	·0440	·0472	4·81	·0128	·075	5·04	·0647	·0624	·293	·213	− 24	·222
− 20	0				− ·0027											
− 10	·214	1·290	·271	·0619	·0041	·0463	4·74	·0130	·077	5·05	·0659	·0636	·294	·216	− 9	·224
− 6	0				− ·0018											
+ 3	·215	1·300	·274	·0626	·0459	·0468	4·79	·0130	·078	5·05	·0659	·0635	·294	·216	+ 3	·222
5	0				·0000											
13	·214	1·292	·271	·0619	·0463	·0463	4·74	·0130	·079	5·06	·0660	·0636	·295	·215	13	·220
15	0				·0000											
21	·214	1·295	·272	·0619	·0472	·0468	4·79	·0129	·079	5·06	·0655	·0630	·295	·213	21	·217
21	0				·0007											

Duration of experiment, 7 hours 20 minutes.

* See note on p. 407.

CADMIUM ROD (Second Experiment).

$a_2=2\cdot34$ centims., approx. $k=\cdot217$, therefore $b'=\cdot29$, $x_A=\cdot39$, $x_B=3\cdot31$, $x_C=3\cdot70$, $x_{C'}=3\cdot89$ centims., $s=1\cdot83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	R_B-R_A, ohms.	Differences, ohms.	Pt. temp. differences.	Heat temp. difference.	$\sqrt{6\cdot85\frac{h}{k}}$.	$x_BS_B-x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H temp. of rod.	k_H.
°C.															°C.	
+ 20	0				+ ·0044											
22	·213	1·300	·272	·0619	·0339	·0296	3·03	·0205	·079	2·96	·0604	·0588	·280	·210	+ 22	·213
20	0				·0042											
− 203	0				− ·0034											
− 181	·217	1·250	·268	·0618	·0260	·0295	3·02	·0205	·062	2·94	·0603	·0593	·275	·216	− 168	·243
− 177	0				− ·0035											
− 165	·217	1·260	·270	·0620	·0265	·0298	3·05	·0204	·063	2·94	·0600	·0589	·275	·214	− 153	·238
− 161	0				− ·0032											
− 151	·217	1·260	·270	·0620	·0272	·0301	3·08	·0202	·065	2·94	·0596	·0585	·276	·212	− 141	·235
− 149	0				− ·0026											
− 140	·216	1·265	·269	·0618	·0277	·0301	3·08	·0201	·066	2·95	·0593	·0582	·276	·211	− 131	·233
− 139	0				− ·0022											
− 133	0				− ·0028											
− 122	·220	1·314	·284	·0652	·0288	·0313	3·20	·0204	·067	2·95	·0602	·0591	·276	·214	− 115	·234
− 120	0				− ·0022											
− 110	·219	1·320	·284	·0652	·0293	·0313	3·20	·0204	·068	2·95	·0602	·0590	·276	·214	− 104	·233
− 107	0				− ·0019											
− 96	·219	1·320	·284	·0652	·0297	·0313	3·20	·0204	·069	2·95	·0602	·0590	·277	·213	− 91	·230
− 94	0				− ·0014											
− 83	·219	1·330	·286	·0657	·0303	·0314	3·21	·0205	·070	2·95	·0605	·0593	·277	·214	− 79	·230
− 80	0				− ·0009											
− 71	·217	1·320	·281	·0642	·0303	·0310	3·17	·0203	·071	2·95	·0599	·0586	·277	·212	− 68	·226
− 68	0				− ·0005											
− 62	0				− ·0017											
− 50	·217	1·312	·279	·0638	·0295	·0308	3·15	·0203	·072	2·95	·0599	·0586	·278	·211	− 48	·223
− 46	0				− ·0009											
− 36	·217	1·320	·281	·0642	·0302	·0308	3·15	·0204	·074	2·95	·0602	·0588	·278	·211	− 35	·221
− 33	0				− ·0004											
− 22	·217	1·314	·279	·0638	·0310	·0309	3·16	·0202	·075	2·95	·0596	·0582	·279	·209	− 21	·217
− 19	0				·0006											
− 10	·217	1·320	·281	·0642	·0314	·0306	3·13	·0206	·077	2·95	·0608	·0593	·279	·212	− 10	·219
− 6	0				·0010											
+ 2	·217	1·320	·281	·0642	·0314	·0303	3·10	·0208	·078	2·95	·0616	·0601	·280	·215	+ 2	·221
3	0				·0013											
10	·216	1·322	·280	·0640	·0321	·0306	3·13	·0205	·079	2·96	·0607	·0591	·280	·211	10	·216
12	0				·0017											
19	·216	1·322	·280	·0637	·0324	·0304	3·11	·0205	·079	2·96	·0607	·0591	·280	·210	19	·214
20	0				·0022											

Duration of experiment, 5 hours.

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* See note on p. 407.

ALUMINIUM ROD.

Turned from a Rod supplied by Messrs. JOHNSON and MATTHEY as ·99 Al. Density at 20° C. = 2·70.

$a_2 = 4{\cdot}38$ centims., approx. $k = {\cdot}48$, therefore $b' = {\cdot}31$, $x_A = {\cdot}41$, $x_B = 5{\cdot}41$, $x_C = 5{\cdot}72$, $x_{C'} = 5{\cdot}93$ centims., $s = 1{\cdot}83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat temp. difference.	$\sqrt{6{\cdot}85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 17	0				+ ·0034											
19	·250	1·52	·372	·0849	·0335	·0300	3·07	·0277	·053	5·08	·141	·138	·281	·491	+ 19	·500
19	0				·0035											
− 195	0				·0000											
− 179	·258	1·48	·373	·0862	·0362	·0322	3·30	·0261	·044	5·05	·132	·130	·276	·471	− 166	·528
− 176	0				·0048											
− 166	·257	1·48	·374	·0861	·0388	·0333	3·41	·0252	·044	5·05	·127	·125	·276	·453	− 154	·508
− 164	0				·0063											
− 155	0				·0009											
− 146	·257	1·49	·374	·0861	·0350	·0339	3·47	·0248	·045	5·05	·125	·123	·277	·444	− 136	·492
− 146	0				·0013											
− 137	·257	1·49	·374	·0861	·0354	·0339	3·47	·0248	·046	5·05	·125	·123	·277	·444	− 128	·490
− 136	0				·0017											
− 130	·257	1·50	·377	·0868	·0357	·0339	3·47	·0250	·046	5·05	·126	·124	·277	·448	− 122	·492
− 127	0				·0019											
− 121	·256	1·50	·375	·0863	·0358	·0339	3·47	·0248	·046	5·05	·125	·123	·277	·444	− 114	·486
− 121	0				·0020											
− 116	0				·0000											
− 106	·262	1·56	·400	·0920	·0344	·0349	3·57	·0258	·047	5·05	·130	·128	·278	·461	− 100	·501
− 104	0				− ·0010											
− 93	·263	1·58	·407	·0936	·0343	·0353	3·61	·0259	·047	5·05	·131	·129	·278	·464	− 88	·501
− 90	0				− ·0010											
− 77	·263	1·58	·407	·0936	·0339	·0349	3·57	·0262	·048	5·06	·133	·131	·278	·472	− 73	·496
− 75	0				− ·0009											
− 66	·263	1·59	·409	·0936	·0339	·0346	3·54	·0264	·049	5·06	·134	·132	·279	·474	− 63	·497
− 63	0				− ·0006											
− 53	0				− ·0017											
− 40	·261	1·576	·402	·0920	·0328	·0339	3·47	·0265	·050	5·06	·134	·132	·280	·472	− 39	·496
− 34	0				− ·0006											
− 23	·260	1·58	·401	·0918	·0325	·0330	3·38	·0272	·050	5·07	·138	·136	·280	·486	− 22	·507
− 19	0				− ·0004											
− 8	·259	1·58	·401	·0918	·0324	·0326	3·34	·0275	·051	5·07	·139	·137	·280	·490	− 8	·507
− 4	0				·0000											
+ 6	·259	1·59	·402	·0920	·0335	·0329	3·37	·0273	·052	5·08	·139	·137	·280	·490	+ 6	·503
9	0				·0013											
17	·259	1·59	·402	·0920	·0337	·0323	3·31	·0278	·053	5·08	·141	·139	·280	·497	17	·508
17	0				·0017											
24	·259	1·59	·403	·0919	·0339	·0320	3·28	·0280	·053	5·08	·142	·139	·280	·497	24	·505
25	0				·0021											

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* See note on p. 407.

TIN ROD.

Turned from a Bar of Pure Tin supplied by Messrs. KAHLBAUM. Density at 21° C. = 7·28.

$a_2 = 4·50$ centims., approx. $k = ·16$, therefore $b' = ·27$, $x_A = ·37$, $x_B = 5·41$, $x_C = 5·78$, $x_{C'} = 5·98$ centims.; $s = 1·83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	$\frac{\text{Heat}}{\text{temp. difference.}}$	$\sqrt{6·85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 23	0				+ ·0034											
27	·183	1·100	·197	·0449	·0493	·0460	4·71	·00953	·093	5·27	·0503	·0477	·308	·155	+ 27	·157
25	0				·0032											
− 200	0				− ·0049											
− 186	·185	1·057	·192	·0445	·0380	·0428	4·38	·01020	·073	5·18	·0529	·0513	·292	·175	− 174	·197
− 179	0				− ·0047											
− 169	·185	1·060	·193	·0445	·0396	·0439	4·49	·00990	·074	5·19	·0514	·0498	·293	·170	− 157	·190
− 166	0				− ·0040											
− 153	·185	1·061	·193	·0444	·0407	·0442	4·52	·00984	·075	5·19	·0511	·0494	·293	·168	− 143	·187
− 135	0				− ·0027											
− 126	·185	1·061	·193	·0444	·0419	·0448	4·59	·00968	·078	5·20	·0504	·0486	·296	·164	− 118	·180
− 124	0				− ·0030											
− 116	0				− ·0064											
− 106	·186	1·097	·200	·0460	·0400	·0465	4·76	·00967	·080	5·21	·0504	·0485	·297	·163	− 110	·178
− 96	0				− ·0066											
− 86	·187	1·104	·203	·0466	·0412	·0475	4·86	·00959	·082	5·22	·0501	·0481	·298	·161	− 82	·173
− 79	0				− ·0060											
− 68	·187	1·110	·204	·0467	·0419	·0477	4·88	·00957	·083	5·22	·0500	·0480	·299	·160	− 65	·171
− 62	0				− ·0056											
− 47	·187	1·117	·205	·0469	·0428	·0481	4·92	·00953	·085	5·23	·0499	·0478	·301	·159	− 45	·168
− 42	0				− ·0050											
− 38	·187	1·121	·206	·0471	·0436	·0481	4·92	·00957	·087	5·24	·0502	·0479	·302	·158	− 30	·165
− 24	0				− ·0041											
− 18	0				− ·0066											
− 8	·185	1·111	·202	·0462	·0421	·0477	4·88	·00947	·089	5·25	·0497	·0473	·304	·155	− 8	·160
+ 1	0				− ·0045											
12	·185	1·120	·203	·0462	·0444	·0477	4·88	·00947	·092	5·27	·0499	·0474	·307	·154	+ 14	·157
22	0				− ·0022											
30	·186	1·130	·205	·0467	·0459	·0477	4·88	·00947	·093	5·27	·0499	·0473	·308	·153	30	·155
34	0				− ·0013											

Duration of experiment, 5 hours 20 minutes.

* See note on p. 407.

LEAD ROD.

Turned from a Bar of Pure Lead supplied by Messrs. BAXENDALE, Manchester. Density at 25° C. = 11·29.

$a_2 = 1\cdot90$ centims., approx. $k = \cdot082$, therefore $b' = \cdot23$, $x_A = \cdot33$, $x_B = 2\cdot69$, $x_C = 3\cdot02$, $x_{C'} = 3\cdot17$ centims. $s = 1\cdot83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat / temp. difference.	$\sqrt{6\cdot85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.																
+ 18	0				+ ·0031										° C.	
23	·202	1·225	·242	·0552	·0558	·0526	5·38	·01026	·130	2·42	·0249	·0235	·289	·0814	+ 23	·0828
20	0				·0032											
− 194	0				− ·0064											
− 177	·209	1·200	·246	·0568	·0499	·0559	5·72	·00993	·102	2·39	·0238	·0229	·281	·0816	− 164	·0926
− 179	0				− ·0058											
− 151	·210	1·220	·251	·0577	·0514	·0568	5·81	·00993	·105	2·39	·0238	·0229	·282	·0813	− 141	·0902
− 145	0				− ·0050											
− 129	·210	1·225	·252	·0579	·0527	·0573	5·86	·00988	·109	2·40	·0237	·0227	·283	·0803	− 121	·0882
− 124	0				− ·0042											
− 110	·210	1·230	·253	·0582	·0542	·0580	5·93	·00982	·110	2·40	·0235	·0225	·283	·0796	− 104	·0867
− 107	0				− ·0033											
− 97	·210	1·235	·254	·0584	·0547	·0578	5·92	·00986	·113	2·40	·0237	·0227	·284	·0800	− 92	·0866
− 94	0				− ·0029											
− 82	·210	1·240	·255	·0586	·0555	·0580	5·94	·00987	·115	2·40	·0237	·0226	·285	·0794	− 78	·0853
− 81	0				− ·0021											
− 64	·210	1·245	·257	·0588	·0562	·0580	5·94	·00990	·117	2·40	·0237	·0226	·285	·0794	− 61	·0847
− 64	0				− ·0014											
− 54	·210	1·250	·257	·0588	·0567	·0581	5·95	·00988	·118	2·41	·0238	·0227	·286	·0794	− 52	·0841
− 54	0				− ·0015											
− 48	0				− ·0017											
− 38	·213	1·290	·270	·0618	·0582	·0600	6·14	·01006	·120	2·41	·0243	·0231	·286	·0808	− 37	·0850
− 37	0				− ·0018											
− 26	·212	1·290	·268	·0614	·0582	·0598	6·12	·01003	·122	2·41	·0243	·0231	·287	·0805	− 25	·0841
− 26	0				− ·0014											
− 18	·212	1·290	·268	·0614	·0571	·0588	6·02	·01020	·124	2·41	·0245	·0233	·287	·0812	− 17	·0844
− 18	0				− ·0021											
− 12	0				− ·0021											
− 1	·208	1·264	·258	·0591	·0549	·0563	5·76	·01026	·126	2·41	·0248	·0235	·288	·0816	− 1	·0841
+ 2	0				− ·0008											
11	·207	1·260	·256	·0586	·0554	·0558	5·71	·01026	·128	2·41	·0248	·0235	·289	·0814	+ 11	·0832
11	0				·0000											
19	·2055	1·254	·252	·0577	·0550	·0547	5·60	·01030	·129	2·42	·0249	·0236	·289	·0817	19	·0834
19	0				·0006											
26	·205	1·250	·251	·0574	·0548	·0540	5·53	·01038	·130	2·42	·0249	·0235	·289	·0814	26	·0828
24	0				·0010											

Duration of experiment, 5 hours 30 minutes.

* See note on p. 407.

WROUGHT IRON ROD.

Turned from a Bar of "Best Scrap Iron." Fe = ·9942, C = ·001, Mn = ·0015, Si = ·0013.*
Density at 21° C. = 7·74.

$a_2 = 3{\cdot}80$ centims., approx. $k = {\cdot}14$, therefore $b' = {\cdot}27$, $x_A = {\cdot}37$, $x_B = 4{\cdot}71$, $x_C = 5{\cdot}08$, $x_{C'} = 5{\cdot}26$ centims., $s = 1{\cdot}83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat / temp. difference.	$\sqrt{6{\cdot}85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.†	II.†	III.†	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
− 184	0				− ·0034											
− 172	·173	·990	·169	·0391	·0401	·0422	4·32	·00905	·079	4·45	·0403	·0389	·290	·134	− 160	·150
− 158	0				− ·0007											
− 151	·173	·990	·169	·0389	·0341	·0398	4·07	·00956	·081	4·45	·0425	·0410	·291	·141	− 140	·156
− 144	0				− ·0081											
− 133	·173	·997	·170	·0392	·0321	·0404	4·13	·00949	·083	4·46	·0424	·0408	·292	·139	− 125	·153
− 127	0				− ·0084											
− 116	·171	·990	·167	·0385	·0310	·0392	4·01	·00960	·084	4·47	·0430	·0413	·293	·140	− 109	·153
− 110	0				− ·0079											
− 100	·170	·990	·166	·0382	·0313	·0388	3·97	·00962	·086	4·47	·0430	·0413	·294	·140	− 95	·151
− 96	0				− ·0071											
− 72	0				− ·0056											
− 63	·172	1·012	·171	·0392	·0340	·0398	4·07	·00963	·090	4·48	·0432	·0413	·297	·139	− 60	·148
− 54	0				− ·0059											
− 46	·170	1·005	·168	·0385	·0334	·0388	3·97	·00970	·092	4·49	·0436	·0417	·298	·139	− 44	·146
− 44	0				− ·0048											
− 17	0				− ·0085											
− 1	·172	1·030	·174	·0399	·0319	·0388	3·97	·0101	·097	4·50	·0455	·0434	·301	·144	− 1	·148
+ 2	0				− ·0053											
13	·172	1·035	·175	·0400	·0343	·0387	3·96	·0101	·098	4·51	·0456	·0434	·302	·143	+ 13	·146
16	0				− ·0036											

Duration of experiment, 5 hours.

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* I have to thank my colleague, Professor J. T. HEWITT, for the analysis of this specimen.

† See note on p. 407.

NICKEL ROD.

Turned from a Bar supplied by Messrs. JOHNSON and MATTHEY as ·99 Ni. Density at 21° C. = 8·80.

a_2=3·86 centims., approx. k=·14, therefore b'=·27, x_A=·37, x_B=4·77, x_C=5·14, $x_{C'}$=·32 centims., s=1·83 sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	$\frac{\text{Heat}}{\text{temp. difference}}$.	$\sqrt{6 \cdot 85 \frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
°C.															°C.	
+ 28	·190	1·150	·215	·0490	+ ·0542	·0507	5·19	·00944	·099	4·58	·0432	·0409	·303	·136	+ 28	·138
25	0				+ ·0035											
− 183	0				− ·0100											
− 170	·191	1·096	·206	·0475	·0504	·0598	6·12	·00775	·085	4·53	·0352	·0338	·294	·115	− 159	·129
− 163	0				− ·0089											
− 150	·192	1·101	·208	·0478	·0500	·0582	5·96	·00802	·088	4·54	·0365	·0350	·296	·116	− 143	·131
− 146	0				− ·0076											
− 135	·192	1·110	·209	·0480	·0497	·0574	5·87	·00817	·089	4·54	·0371	·0355	·296	·120	− 126	·132
− 132	0				− ·0078											
− 120	·1916	1·110	·209	·0480	·0499	·0583	5·97	·00803	·091	4·55	·0366	·0349	·297	·118	− 113	·129
− 116	0				− ·0090											
− 102	·191	1·116	·208	·0478	·0457	·0546	5·59	·00854	·086	4·53	·0387	·0370	·294	·126	− 97	·136
− 98	0				− ·0088											
− 84	·191	1·120	·210	·0483	·0456	·0540	5·53	·00873	·087	4·53	·0396	·0378	·296	·128	− 80	·138
− 80	0				− ·0080											
− 68	·191	1·127	·212	·0485	·0459	·0539	5·52	·00878	·089	4·54	·0399	·0381	·297	·128	− 65	·137
− 64	0				− ·0079											
− 50	0				− ·0113											
− 31	·192	1·150	·217	·0496	·0437	·0531	5·44	·00912	·093	4·56	·0416	·0396	·299	·133	− 30	·139
− 28	0				− ·0084											
− 15	·191	1·156	·217	·0496	·0448	·0522	5·34	·00930	·094	4·56	·0424	·0403	·299	·136	− 15	·140
− 13	0				− ·0064											
− 1	·191	1·160	·218	·0498	·0466	·0516	5·28	·00943	·096	4·57	·0431	·0409	·301	·137	− 1	·141
+ 2	0				− ·0038											
11	·191	1·160	·218	·0498	·0481	·0511	5·23	·00954	·098	4·58	·0437	·0415	·302	·138	+ 11	·141
14	0				− ·0022											

Duration of experiment, 5 hours 30 minutes.

* See note on p. 407.

STEEL ROD.

Turned from a Bar of High Carbon Steel, known as "Silver Steel," containing approximately 1 per cent. of Carbon.
Density at 24° C. = 7·84.

$a_2 = 4·30$ centims., approx. $k = ·11$, therefore $h' = ·26$, $x_A = ·36$, $x_B = 5·18$, $x_C = 5·44$, $x_{C'} = 5·61$ centims., $s = 1·83$ sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat temp. difference.	$\sqrt{6·85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 23	·170	1·03	·172	·0393	+ ·0550	·0523	5·36	·00734	·111	5·13	·0377	·0356	·319	·112	+ 23	·114
19	0				+ ·0027											
− 131	0				− ·0035											
− 114	·169	·99	·165	·0380	·0485	·0541	5·54	·00686	·095	5·03	·0345	·0329	·304	·108	− 107	·117
− 117	0				− ·0077											
− 96	·168	·99	·164	·0378	·0470	·0545	5·58	·00678	·096	5·04	·0342	·0325	·306	·106	− 91	·114
− 98	0				− ·0073											
− 79	·169	1·00	·167	·0385	·0468	·0540	5·53	·00696	·099	5·05	·0352	·0334	·308	·109	− 75	·116
− 81	0				− ·0070											
− 64	·171	1·01	·171	·0394	·0470	·0533	5·46	·00722	·100	5·06	·0365	·0347	·309	·112	− 61	·119
− 42	0				− ·0058											
− 28	·168	1·00	·166	·0381	·0460	·0508	5·20	·00733	·105	5·07	·0372	·0352	·314	·112	− 27	·117
− 31	0				− ·0042											
− 13	·167	·98	·162	·0372	·0460	·0494	5·06	·00736	·106	5·08	·0374	·0353	·315	·112	− 13	·116
− 18	0				− ·0029											
− 3	·167	·99	·162	·0372	·0472	·0494	5·06	·00736	·108	5·09	·0375	·0354	·315	·113	− 3	·115
− 9	0				− ·0015											
+ 4	·167	·99	·162	·0372	·0483	·0493	5·05	·00738	·109	5·10	·0377	·0356	·317	·112	+ 4	·115
− 3	0				− ·0005											
+ 9	·168	1·00	·164	·0374	·0487	·0490	5·02	·00746	·110	5·10	·0381	·0360	·318	·112	+ 9	·116
+ 2	0				·0000											
− 199	0				− ·0012											
− 184	·169	·96	·160	·0370	·0541	·0572	5·85	·00632	·088	4·99	·0315	·0301	·299	·101	− 168	·113
− 185	0				− ·0042											
− 187	0				− ·0109											
− 150	·168	·96	·158	·0364	·0419	·0554	5·67	·00642	·090	5·01	·0322	·0407	·301	·102	− 140	·113
− 145	0				− ·0148											
− 120	·169	·98	·162	·0373	·0414	·0554	5·67	·00658	·094	5·03	·0331	·0315	·304	·104	− 113	·112
− 118	0				− ·0132											
− 96	·170	·99	·164	·0378	·0413	·0548	5·61	·00674	·097	5·04	·0340	·0323	·306	·106	− 91	·114
− 95	0				− ·0139											
− 75	·170	·99	·164	·0378	·0415	·0538	5·51	·00686	·099	5·15	·0347	·0329	·308	·107	− 71	·114
− 75	0				− ·0107											

Duration of experiment, 1 hour + 6 hours + 6 hours.

BRASS ROD.

Turned from a Rod of Composition ·70 Cu, ·30 Zn, approx. Density at 22° C. = 8·44.

a_2 = 4·11 centims., approx. k = ·16 to ·26, therefore b' = ·282 to ·290, taken = ·285, x_A = ·39, x_B = 5·07, x_C = 5·45, $x_{C'}$ = 5·64 centims., s = 1·83 sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat temp. difference.	$\sqrt{6 \cdot 85 \frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 20	0				+ ·0033											
23	·202	1·220	·241	·0549	·0368	·0336	3·44	·0160	·073	4·80	·0769	·0745	·289	·258	+ 23	·262
21	0				·0031											
− 189	0				− ·0059											
− 178	·208	1·190	·243	·0561	·0496	·0559	5·72	·0098	·073	4·80	·0471	·0456	·289	·158	− 165	·178
− 174	0				− ·0066											
− 161	·208	1·200	·245	·0563	·0472	·0529	5·41	·0104	·073	4·80	·0498	·0483	·289	·167	− 150	·186
− 157	0				− ·0048											
− 148	·209	1·210	·248	·0570	·0476	·0518	5·30	·0108	·073	4·80	·0517	·0501	·289	·174	− 138	·193
− 145	0				− ·0036											
− 139	0				− ·0061											
− 129	·214	1·265	·266	·0612	·0463	·0528	5·40	·0113	·072	4·80	·0540	·0523	·289	·181	− 121	·199
− 123	0				− ·0068											
− 109	·215	1·280	·270	·0621	·0428	·0496	5·08	·0123	·072	4·80	·0583	·0567	·289	·196	− 103	·212
− 103	0				− ·0069											
− 89	·215	1·282	·271	·0623	·0413	·0477	4·88	·0127	·072	4·80	·0612	·0594	·289	·206	− 85	·221
− 83	0				− ·0059											
− 72	·215	1·290	·272	·0623	·0405	·0459	4·70	·0132	·072	4·80	·0635	·0616	·289	·213	− 69	·228
− 66	0				− ·0049											
− 52	0				− ·0093											
− 36	·212	1·270	·264	·0604	·0334	·0414	4·24	·0142	·072	4·80	·0683	·0662	·289	·229	− 35	·240
− 27	0				− ·0067											
− 13	·212	1·272	·264	·0604	·0332	·0390	3·99	·0151	·072	4·80	·0725	·0703	·289	·243	− 13	·252
− 4	0				− ·0049											
+ 8	·211	1·280	·266	·0609	·0346	·0385	3·94	·0154	·072	4·80	·0740	·0717	·289	·248	+ 8	·253
14	0				− ·0029											
25	·211	1·282	·266	·0606	·0346	·0369	3·78	·0160	·073	4·80	·0769	·0745	·289	·257	25	·261
28	0				− ·0018											

Duration of experiment, 5 hours.

* See note on p. 407.

GERMAN SILVER ROD.

Turned from a Rod supplied by Messrs. JOHNSON and MATTHEY of Composition ·62 Cu, ·15 Ni, ·22 Zn, approx.
Density at 22° C. = 8·67.

a_2 = 4·26 centims., approx. k = ·04 to ·06, therefore b' = ·22, x_A = ·32, x_B = 5·02, x_C = 5·34, $x_{C'}$ = 5·49 centims.,
s = 1·83 sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat temp. difference.	$\sqrt{6\cdot 85\frac{h}{k}}$	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 21	0				+ ·0031											
25	·142	·854	·119	·0272	·0614	·0582	5·96	·00456	·152	5·20	·0237	·0212	·361	·0588	+ 25	·0597
22	0				·0033											
− 195	0				− ·0148											
− 176	·146	·834	·120	·0278	·0773	·0934	9·56	·00291	·145	5·16	·0150	·0134	·351	·0382	− 163	·0428
− 165	0				− ·0172											
− 144	·146	·837	·120	·0276	·0704	·0855	8·76	·00318	·145	5·16	·0162	·0145	·351	·0413	− 134	·0456
− 142	0				− ·0133											
− 126	·146	·841	·121	·0279	·0716	·0878	8·99	·00310	·146	5·17	·0160	·0142	·353	·0402	− 118	·0440
− 120	0				− ·0191											
− 100	·146	·846	·122	·0281	·0606	·0793	8·12	·00346	·147	5·17	·0179	·0161	·354	·0454	− 95	·0493
− 90	0				− ·0185											
− 74	·146	·851	·122	·0281	·0591	·0769	7·87	·00357	·149	5·18	·0185	·0165	·358	·0460	− 70	·0493
− 63	0				− ·0172											
− 46	·146	·860	·124	·0284	·0578	·0728	7·45	·00381	·149	5·18	·0197	·0175	·358	·0490	− 44	·0517
− 40	0				− ·0128											
− 26	·146	·861	·124	·0284	·0588	·0692	7·08	·00401	·150	5·18	·0207	·0184	·358	·0515	− 25	·0538
− 22	0				− ·0085											
− 11	·146	·864	·124	·0284	·0597	·0662	6·78	·00419	·151	5·20	·0217	·0193	·361	·0536	− 11	·0554
− 10	0				− ·0046											
− 5	0				− ·0085											
+ 7	·148	·901	·131	·0300	·0614	·0676	6·92	·00432	·151	5·20	·0225	·0198	·361	·0549	+ 7	·0563
8	0				− ·0039											
16	·148	·901	·131	·0300	·0622	·0649	6·64	·00451	·150	5·18	·0234	·0208	·358	·0582	16	·0594
17	0				− ·0019											

Duration of experiment, 8 hours 20 minutes.

* See note on p. 407.

Platinoid Rod.

Turned from a Rod supplied by the London Electric Wire Company. Composition approximately that of German Silver. Density at 22° C. = 8·66.

a_2 = 1·51 centims., approx. k = ·04 to ·06, therefore b' = ·21, x_A = ·31, x_B = 2·24, x_C = 2·55, $x_{C'}$ = 2·69 centims., s = 1·83 sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat temp. difference.	$\sqrt{6\cdot85\,\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
−186	0				−·0134											
−170	·181	1·040	·184	·0426	·0627	·0757	7·75	·00549	·150	1·97	·0109	·0102	·288	·0354	−158	·0397
−164	0				−·0125											
−149	·181	1·050	·186	·0428	·0605	·0722	7·39	·00579	·150	1·97	·0115	·0107	·288	·0371	−139	·0412
−145	0				−·0110											
−129	·181	1·054	·187	·0431	·0579	·0682	6·98	·00617	·150	1·97	·0122	·0114	·288	·0395	−121	·0435
−124	0				−·0097											
−108	·181	1·060	·188	·0433	·0564	·0654	6·69	·00646	·150	1·97	·0128	·0120	·288	·0416	−102	·0453
−103	0				−·0082											
−90	·181	1·064	·189	·0435	·0549	·0623	6·38	·00681	·150	1·97	·0135	·0126	·288	·0437	−86	·0471
−86	0				−·0066											
−79	0				−·0088											
−65	·183	1·096	·197	·0452	·0521	·0601	6·15	·00733	·150	1·97	·0145	·0136	·288	·0474	−62	·0505
−61	0				−·0071											
−45	·179	1·080	·190	·0436	·0488	·0550	5·63	·00774	·150	1·97	·0153	·0143	·288	·0498	−43	·0525
−30	0				−·0054											
−26	·179	1·086	·191	·0438	·0481	·0525	5·39	·00815	·150	1·97	·0161	·0151	·288	·0526	−25	·0549
−24	0				−·0035											
−12	·179	1·090	·191	·0438	·0470	·0498	5·10	·00858	·150	1·97	·0170	·0159	·288	·0553	−12	·0575
−10	0				−·0021											
−2	0				−·0054											
+7	·177	1·070	·186	·0427	·0438	·0478	4·89	·00872	·150	1·97	·0172	·0161	·288	·0560	+7	·0575
10	0				−·0025											
21	·176	1·070	·185	·0422	·0432	·0449	4·60	·00917	·150	1·97	·0181	·0170	·288	·0591	21	·0602
22	0				−·0009											
30	·174	1·060	·181	·0413	·0426	·0428	4·38	·00942	·150	1·97	·0186	·0175	·288	·0609	31	·0616
31	0				+·0005											

Duration of experiment, 6 hours 20 minutes.

* See note on p. 407.

MANGANINE ROD.

Turned from a Bar supplied by Messrs. W. T. GLOVER. Composition ·84 Cu, ·04 Ni, ·12 Mn, approx.
Density at 22° C. = 8·42.

a_2 = 1·90 centims., approx. k = ·032 to ·052, therefore b' = ·20, x_A = ·30, x_B = 2·60, x_C = 2·90, $x_{C'}$ = 3·03 centims.,
s = 1·83 sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	$\frac{\text{Heat}}{\text{temp. difference}}$.	$\sqrt{6\cdot85\frac{h}{k}}$.	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
°C.															°C.	
– 190	0				– ·0168											
– 169	·180	1·037	1·84	·0426	·0807	·0972	9·95	·00428	·162	2·38	·0101	·0094	·298	·0316	– 157	·0353
– 165	0				– ·0161											
– 145	·180	1·045	1·85	·0426	·0774	·0927	9·49	·00448	·162	2·38	·0107	·0098	·298	·0329	– 135	·0363
– 138	0				– ·0145											
– 117	·180	1·050	1·85	·0426	·0746	·0877	8·98	·00474	·161	2·38	·0113	·0103	·298	·0346	– 110	·0377
– 110	0				– ·0117											
– 94	·180	1·054	1·86	·0428	·0724	·0833	8·53	·00501	·161	2·38	·0119	·0109	·298	·0366	– 89	·0396
– 92	0				– ·0101											
– 76	·179	1·060	1·86	·0428	·0709	·0798	8·17	·00524	·161	2·38	·0125	·0114	·298	·0382	– 72	·0409
– 73	0				– ·0077											
– 58	·179	1·062	1·87	·0429	·0686	·0756	7·74	·00554	·161	2·38	·0132	·0121	·298	·0406	– 56	·0431
– 53	0				– ·0064											
– 46	0				– ·0092											
– 31	·185	1·120	2·03	·0464	·0678	·0758	7·76	·00598	·161	2·38	·0143	·0131	·298	·0440	– 30	·0460
– 28	0				– ·0067											
– 14	·185	1·120	2·03	·0464	·0660	·0718	7·35	·00632	·161	2·38	·0150	·0138	·298	·0465	– 14	·0483
– 13	0				– ·0050											
– 1	·185	1·126	2·05	·0469	·0654	·0690	7·16	·00655	·162	2·38	·0156	·0144	·298	·0486	– 1	·0501
– 1	0				– ·0023											
+ 8	·185	1·130	2·05	·0469	·0661	·0678	6·94	·00676	·162	2·38	·0161	·0149	·298	·0502	+ 8	·0515
7	0				– ·0011											
16	·184	1·130	2·04	·0465	·0652	·0658	6·73	·00691	·162	2·38	·0164	·0151	·298	·0509	16	·0520
15	0				– ·0002											
22	·184	1·130	2·04	·0465	·0650	·0648	6·63	·00702	·163	2·38	·0167	·0154	·298	·0519	22	·0528
19	0				+ ·0007											

Duration of experiment, 7 hours.

* See note on page 407.

Lipowitz Alloy Rod.

Turned from a Bar Cast from Sample of Alloy supplied by Messrs. **Kahlbaum**. Approx. Composition ·50 Bi, ·25 Pb, ·14 Sn, ·11 Cd. Density at 20° C. = 9·66. Melting-point 65° C.

a_2 = 1·85 centims., approx. k = ·038 to ·044; therefore b' = ·185, x_A = ·29, x_B = 2·51, x_C = 2·80, $x_{C'}$ = 2·92 centims.
s = 1·83 sq. centims.

Mean Pt. temp. of rod.	Amp.	Volts.	Watts on sleeve.	Heat to rod, gram.-degrees per sec.	$R_B - R_A$, ohms.	Differences, ohms.	Pt. temp. differences.	Heat / temp. difference.	$\sqrt{6\cdot85\frac{h}{k}}$	$x_BS_B - x_AS_A$.	I.*	II.*	III.*	k_P.	Mean H. temp. of rod.	k_H.
° C.															° C.	
+ 18	0				+ ·0035											
22	·160	·967	·152	·0346	·0575	·0539	5·52	·00626	·177	2·30	·0144	·0131	·302	·0433	+ 22	·0440
19	0				·0037											
− 192	0				− ·0100											
− 175	·165	·942	·154	·0355	·0578	·0676	6·92	·00512	·150	2·28	·0117	·0109	·292	·0374	− 162	·0418
− 170	0				− ·0097											
− 156	·165	·950	·154	·0354	·0584	·0677	6·93	·00510	·153	2·28	·0116	·0108	·293	·0369	− 145	·0409
− 154	0				− ·0089											
− 141	·166	·960	·157	·0360	·0590	·0673	6·89	·00522	·155	2·29	·0120	·0112	·293	·0383	− 132	·0422
− 139	0				− ·0078											
− 126	·166	·960	·157	·0360	·0591	·0663	6·79	·00530	·157	2·29	·0122	·0113	·294	·0385	− 118	·0421
− 123	0				− ·0067											
− 112	0				− ·0080											
− 97	·166	·982	·161	·0370	·0681	·0653	6·68	·00553	·161	2·29	·0127	·0117	·296	·0395	− 92	·0428
− 94	0				− ·0065											
− 80	·166	·990	·162	·0372	·0587	·0647	8·82	·00561	·163	2·29	·0129	·0119	·297	·0400	− 76	·0429
− 76	0				− ·0056											
− 63	·166	·990	·162	·0370	·0587	·0639	6·54	·00565	·165	2·29	·0130	·0120	·297	·0404	− 60	·0428
− 60	0				− ·0047											
− 43	·166	·995	·163	·0373	·0583	·0623	6·38	·00584	·167	2·30	·0134	·0123	·298	·0412	− 41	·0434
− 41	0				− ·0036											
− 29	·165	1·000	·162	·0370	·0584	·0616	6·30	·00587	·169	2·30	·0135	·0124	·298	·0416	− 28	·0435
− 24	0				− ·0029											
− 18	0				− ·0040											
− 6	·162	·977	·156	·0357	·0526	·0563	5·76	·00619	·173	2·30	·0143	·0131	·300	·0436	− 6	·0451
− 4	0				− ·0034											
+ 7	·160	·980	·154	·0352	·0545	·0567	5·80	·00606	·175	2·30	·0140	·0128	·301	·0425	+ 7	·0436
6	0				− ·0008											
15	·161	·977	·155	·0353	·0537	·0543	5·56	·00634	·176	2·30	·0146	·0134	·301	·0445	15	·0455
14	0				− ·0004											
22	·160	·972	·153	·0348	·0534	·0537	5·50	·00632	·177	2·30	·0146	·0133	·302	·0441	22	·0449
22	0				− ·0002											

Duration of experiment, 5 hours 40 minutes.

* See note on p. 407.

The results of the observations are embodied in the curves on the opposite page.

From the smooth curves drawn as nearly as possible through the points given by the observations, the table on p. 426 of values of the conductivities at various temperatures has been constructed.

Discussion of the Thermal Conductivity Results.

An inspection of the curves of results over the temperature range −170° C. to +30° C., to which for comparison the results obtained by Jäger and Diesselhorst* at 18° C. and 100° C. have been added, shows that over the whole range from −170° C. to +100° C. the thermal conductivity of a pure metal changes comparatively little. As to the character and magnitude of the small rates of change of conductivity with temperature at 18° C., the two sets of experiments are in close agreement throughout. As the temperature rises there is a slight decrease in the conductivity of zinc, copper, iron, cadmium, tin, and lead over the range covered by the experiments. The absolute values of the conductivity at 18° C., given by the present experiments, agree closely with those given for these metals at this temperature by Jäger and Diesselhorst, except in the case of cadmium, for which the present value of k at 18° C. is about 2 per cent. less than that obtained by Jäger and Diesselhorst. Silver appears to have a maximum conductivity at about −90° C., and to decrease very slightly in conductivity up to +100° C. The value of k at 18° C., according to the present experiments, is about 3 per cent. less than that of Jäger and Diesselhorst. Steel shows a slight tendency to a maximum about −50° C., the change with temperature at 18° C. agreeing with that found by Jäger and Diesselhorst, although the absolute value at 18° C. is about 5 per cent. higher than for their steel. Aluminium has a minimum conductivity about −110° C., and a rate of change with temperature about 18° C., which agrees with that found by Jäger and Diesselhorst, although the absolute value is about 4 per cent. higher than theirs.

The alloys tested all increase in conductivity with increase of temperature. In the case of manganine the absolute value and the rate of increase with temperature at 18° C. agree with those given by Jäger and Diesselhorst.

When the slight unavoidable differences in purity of the specimens used by Jäger and Diesselhorst and by myself are taken into account, the close agreement between the results obtained by methods which differ so materially from each other must be considered most satisfactory, for not only have we possible differences in chemical composition to contend with, but, according to the researches of Beilby,† for each

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* W. Jäger and H. Diesselhorst, 'Wissenschaftl. Abhandl. d. Phys.-Techn. Reichsanstalt,' 3, p. 270, (1900). In cases where they give two or more values for the same metal, that value has been used to which they attach the greatest weight.

† 'Phil. Mag.,' 8, p. 258 (1904); 'Roy. Soc. Proc.,' A, 76, p. 462 (1906), and 79, p. 463 (1907).

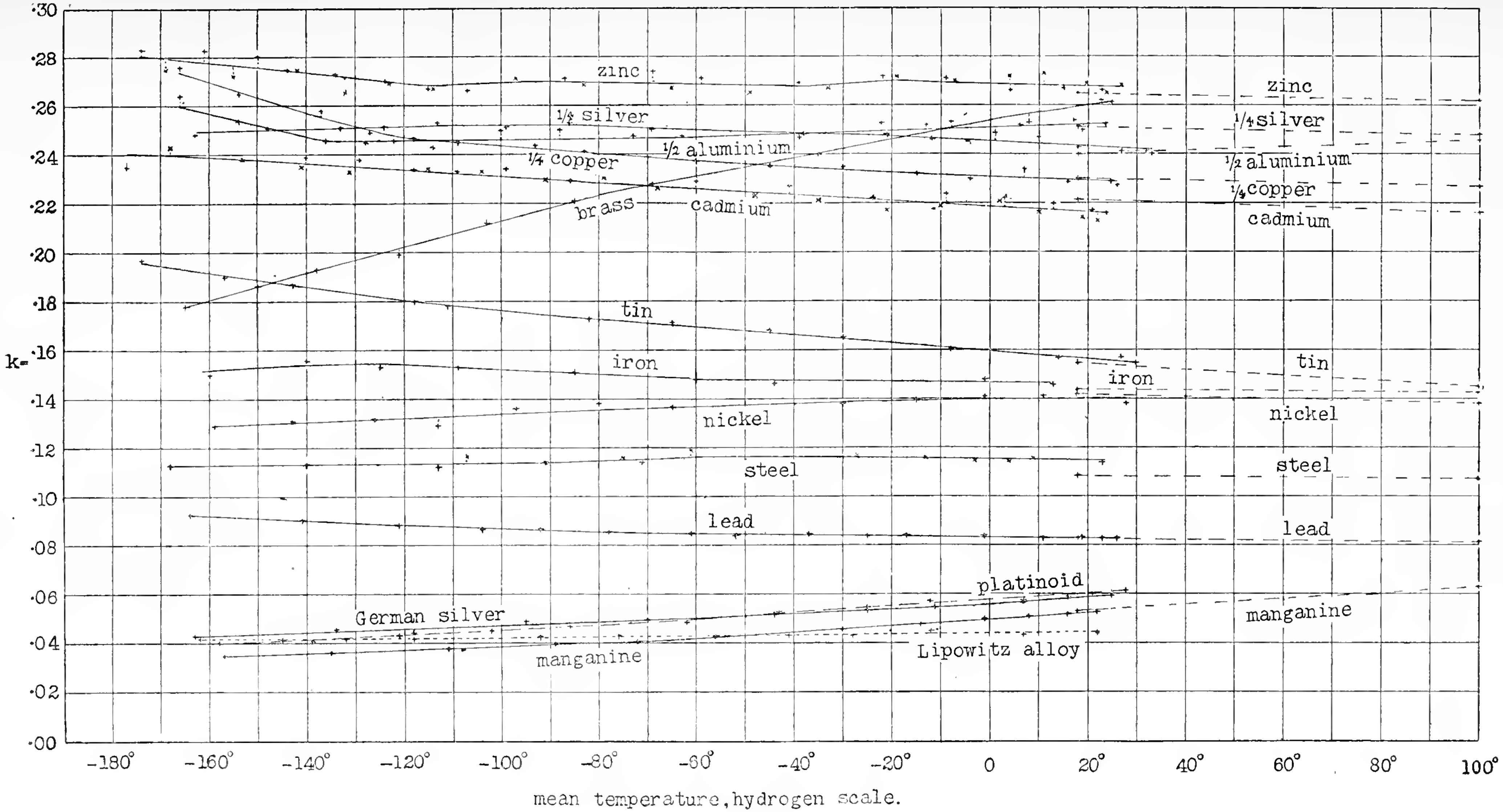

Fig. 3.

Curves of variation of thermal conductivities k of pure metals and alloys with temperature.

Observed values are indicated by crosses, thus :— +. Where a second experiment has been performed, in general with a shorter length of the rod, the observations are indicated thus :— ×.

The dotted lines to the right join the values given by JÄGER and DIESSELHORST for the conductivities at 18° and 100° C. respectively.

For silver and copper the values plotted are $k/4$, and for aluminium $k/2$, as indicated.

TABLE of Thermal Conductivities of pure Metals and Alloys between −170° and +18° C., as deduced from the present Experiments, compared with those at 18° and 100° C. given by JÄGER and DIESSELHORST as the results of their Experiments.

Substance.	From the present experiments.											From JÄGER and DIESSELHORST'S experiments.	
	Chemical and physical state.	At −170° C.	At −160° C.	At −150° C.	At −125° C.	At −100° C.	At −75° C.	At −50° C.	At −25° C.	At 0° C.	At +18° C.	At +18° C.	At +100° C.	Chemical and physical state.
Copper	Pure soft drawn	(1·112)	1·079	1·054	·996	·973	·958	·944	·932	·924	·916	·918	·908	Pure
Silver	·999 Ag	(·996)*	·998	1·000	1·005	1·008	1·004	·997	·997	·981	·974	1·006	·992	·9998 Ag
Zinc	Pure re-distilled cast	·280	·278	·276	·270	·271	·269	·268	·269	·269	·268	·265	·262	Pure cast
Cadmium . . .	,, ,, ,,	·240	·239	·238	·234	·231	·227	·225	·222	·219	·217	·222	·216	,,
Aluminium . .	·99 Al	(·524)	·514	·508	·491	·492	·493	·496	·499	·502	·504	·480	·492	·99 Al
Tin	Pure cast	·195	·192	·189	·182	·176	·172	·168	·164	·160	·157	·155	·145	Pure wire
Lead	Pure	(·093)	·092	·091	·089	·087	·085	·085	·084	·084	·083	·083	·082	Pure
Iron	·994 Fe, ·0015 Mn, ·0013 Ni, approx. ·001 C	(·151)	·152	·153	·154	·152	·150	·148	·147	·147	·147	·144	·143	·9955 Fe
Nickel	·99 Ni	(·128)	·129	·130	·132	·134	·136	·137	·139	·140	·140	·142	·138	·97 Ni
Steel	Approx. ·01 C	(·113)	·113	·113	·113	·114	·115	·116	·116	·116	·115	·108	·107	·01 C
Brass	Approx. ·70 Cu, ·30 Zn	(·175)	·181	·186	·200	·213	·225	·235	·244	·254	·260	—	—	—
German silver .	Approx. ·62 Cu, ·15 Ni, ·22 Zn	(·042)	·043	·044	·045	·047	·049	·051	·054	·056	·059	—	—	—
Platinoid . . .	,, ,, ,, ,,	(·039)	·040	·041	·043	·045	·048	·051	·055	·058	·060	—	—	—
Manganine . .	Approx. ·84 Cu, ·04 Ni, ·12 Mn	(·034)	·035	·035	·037	·039	·041	·043	·046	·050	·052	·053	·063	—
Lipowitz alloy .	Approx. ·50 Bi, ·25 Pb, ·14 Sn, ·11 Cd	(·042)	·042	·042	·042	·042	·043	·043	·044	·044	·044	—	—	—

* The values enclosed in brackets are obtained by a slight extrapolation.

metal there is a hard and a soft state, with different physical properties. If in the future a still closer agreement between the results obtained by different observers is demanded, it will be necessary to specify both chemical composition and microscopic structure of the materials tested.

The fact that the thermal conductivities of most of the pure metals decrease with increase of temperature, while those of all the alloys tested increase with increase of temperature, raises the question whether the increase with temperature observed in the case of aluminium both in Jäger and Diesselhorst's experiments and in the present ones, and in that of nickel in the present experiment, cannot be attributed to small amounts (less than 1 per cent.) of impurity remaining in the specimens tested.

While there is much to be said in favour of this in the two cases mentioned, it seems to me that the apparent existence of a maximum of conductivity of silver, and possibly of steel, and a minimum conductivity of aluminium, shows that we must guard ourselves against stating that the thermal conductivities of all pure metals decrease as the temperature rises, and limit ourselves to the less general statement that the thermal conductivities of most pure metals decrease with rise of temperature over the range −170° C. to +100° C., while those of all the alloys tested increase over the same range of temperature.

On comparing these results with those obtained previously for non-metallic substances,* mostly electrical insulators, it will be seen that on the whole metals and non-metals are affected in the same way by change of temperature, *i.e.*, both tend to conduct heat better at low than at high temperatures, while alloys conduct better at high than at low temperatures, and in this respect resemble glass, the only mixture of non-conductors of electricity which has up to the present been investigated.

Section 2.—The Electrical Conductivity Measurements.

The effect of temperature on the electrical resistivity of the material of each rod was determined by sending an electric current along the rod and through a standard small resistance in series with it. The rod was supported on a pair of knife edges, 4 centims. apart, and the difference of potential between the two was compared with that between the potential terminals of the standard resistance by the method shown in fig. 4.

a is the rod, *b*, *c* two short copper cylinders provided with slightly conical holes into which the ends of the rod were gently forced, *d*, *e* are the knife edges which support the rod and serve as potential terminals, *f* is the standard resistance of 0·000994 or 0·0001182 ohm. The current was supplied from a storage cell *g*, and could be adjusted by means of the resistance *h*.

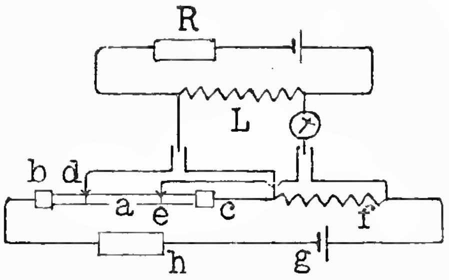

Fig. 4.

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* Lees, 'Phil. Trans. Roy. Soc.,' A, 191, p. 399 (1898); A, 204, p. 433 (1905).

A second circuit, insulated from the first, consisted of a small resistance L provided with potential terminals, a storage cell, and a resistance box R.

One of the potential terminals of L could be connected directly to one of the potential terminals of *f*, or to one of the knife edges on the rod, while the other could be connected through a low-resistance galvanometer to the other terminal of *f*, or to the other knife edge.

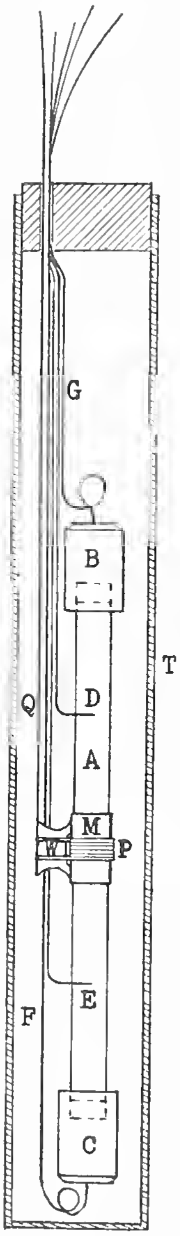

Fig. 5.

In either case the resistance R was adjusted till no current passed through the galvanometer. If R_R is the resistance which gives a balance on the rod and R_S that on the standard resistance, the resistance of the rod between the knife edges is equal to R_S/R_R times that of the standard resistance, the electromotive force in each circuit being supposed constant during the observations, and the resistances of the cell and L being negligible compared to R.

In order to overcome the effects of thermo-electric currents the circuits were made through a "thermo-electric key," which, when up, cuts the cells out of but leaves the galvanometer in circuit. On depressing it, the first operation is to break the galvanometer circuit, then make both cell circuits, and lastly re-make the galvanometer circuit.

The frame supporting the rods during the test is shown in fig. 5. It consists of four strips, G, D, E, F, of sheet copper, 1 centim. wide, 0·08 and 0·05 centim. thick, insulated from each other by strips of mica slightly wider than the copper, the whole shellacked and bound together with shellacked silk thread.

The upper end of each strip is soldered to 30 centims. of copper wire of ·054 centim. diameter, which connects it with the rest of the circuit shown in fig. 4.

The outer copper strips, F and G, end in short lengths of flexible conductor, to the ends of which the copper caps B, C, which fit on to the rod A, are soldered. The middle copper strips are bent at right angles at their lower ends and form the two knife edges D and E in which the rod is supported. To insure good contact, the rod is bound to the frame by a few turns of silk thread passing over it at each knife edge.

The temperature of the rod was measured at the centre of its length by a platinum thermometer P, consisting of about 31 centims. of No. 40 silk-covered platinum wire identical with that used in the thermal conductivity observations, and having a resistance at 0° C. of about 2·73 ohms. This was wound at the centre of a thin ring of mica which just fitted the rods. It was made by winding round one of the rods, whose surface was oiled slightly, a very thin strip of mica which had been shellac varnished, binding wire round it and baking it. On cooling, a ring which stood throughout the experiments was obtained. The ends of the fine platinum wire were soldered to the ends of two lengths each of 33 centims. of double silk-covered copper wire, 0·069 centim. in diameter, Q. In order to prevent strain of the thin wire, the copper wires rested in grooves in the edge of a small block of wood, W, the other edge of which rested on the mica ring, and several turns of thread were taken round ring, block, and leads. The whole was shellac varnished and stoved.

The platinum thermometer formed one arm of a resistance bridge, the equal arms of which each consisted of an ohm coil. The adjustable arm consisted of two resistance boxes with units and tenths, and the dial mercury cup resistance (p. 384) giving hundredths. The current was supplied by a Leclanché cell through a resistance of 5 to 10 ohms, and the galvanometer was a small pointer galvanometer allowing a determination of resistance to 0·002 ohm, and of temperature, therefore, to 0·2° C.

The frame, rod, and thermometer were enclosed in a brass tube T, 15·7 centims. long, 2·2 centims. outside diameter, with walls about 0·05 centim. thick, lined inside with mica. Around this tube a few turns of insulated manganine wire were wound. Through this wire an electric current could be sent if at any time it was necessary to raise the temperature of the apparatus. The rod was not concentric with the tube, owing to the space occupied by the frame. The space between rod and tube was filled with clean sand so as to facilitate communication of heat between the two. The upper end of the tube, out of which the insulated leads passed, was closed by a split cork.

Method of Experimenting.

In making an experiment the following was the routine adopted :—

The rod was first lightly oiled at the centre of its length, and the mica ring of the platinum thermometer slipped over it, the oil assisting the motion and excluding air from the space between rod and inner surface of ring. The excess of oil was then wiped away. The knife edges were then cleaned if necessary. The ends of the rod were next inserted into the end caps and the rod then placed on the knife edges. The threads holding the rod in its place were then wound round it, the rod moved slightly to ensure good electrical contact between it and the knife edges, and the rod and frame placed in the brass tube. The sand was then poured in and the top of the tube closed. The brass tube and contents were then placed in a straight Dewar vacuum vessel, 20 centims. deep, 4 centims. wide, and the top closed by a plug of cotton wool. The various leads were brought to copper mercury cups at which connections were made to the circuits.

The temperature of the rod was determined by balancing the bridge, and the resistance in series with the rod was so adjusted that the values of R (fig. 4) necessary to balance when the supplementary resistance L was connected to the rod and standard resistance f respectively were convenient. After a few minutes' interval, during which any temperature differences in parts of the apparatus had time to disappear, the temperature and the values of R for balance were determined accurately.

Liquid air was then poured into the Dewar tube, and when the temperature had become steady, the observations of temperature and of values of R were repeated.

The liquid air was then poured out of the Dewar tube, and the temperature rose slowly. During the rise several observations of temperature and of R were made at intervals. After three or four observations had been taken the temperature of the apparatus was raised 40° or 50° by sending a current for a few minutes through the manganine wire wound on the outside of the brass tube. When the rate of rise of temperature was again normal, observations were again taken. These steps were repeated till the original temperature of the rod was reached. In no case did the value of the resistivity at the end differ appreciably from its value at the beginning of an experiment.

Reduction of the Electrical Conductivity Observations.

In order to obtain the temperature of the rod from the measurements of the resistance of the platinum thermometer and its leads, we require to know the resistance of the leads and the constants of the thermometer. The resistance of the leads was determined by placing an equal length of the same wire alongside the leads and determining its resistance for various temperatures of the rod during one of the experiments. The values thus found were subtracted from the resistances determined by the bridge in each experiment.

The constants of the platinum coil were found by comparison with the two coils previously used in the heat conductivity measurements. The three coils were made in the same way of the same wire, and the new coil agreed throughout with the old "B" coil. The constants used in the reduction of the resistance measurements to temperature in the former experiments were therefore used in the present case.

As it was not the practice to wait till the temperature was quite steady before observations of temperature and resistance were made, there may be a slight difference of temperature between the rod and thermometer. Attempts were made to determine the magnitude of this difference by raising or lowering the temperature of the zinc rod at about the same rate as was usual in an experiment, *i.e.*, 1° C. per minute, and comparing the results. No difference of temperature of the thermometer so large as the experimental error, ·2° C., could be detected between observations which gave the same value of the resistance of the rod with rising or falling temperature. A rough calculation from the dimensions of the mica ring on which the thermometer was wound showed that the difference of temperature of rod and thermometer could not exceed one-tenth of the change of temperature of the rod in one minute. Whenever in an experiment the rise of temperature has exceeded ·5° C.

per minute, a correction equal to one-tenth the rate of rise has been subtracted from the observed temperature.

The determination of the resistance of the rods depends virtually on the measurement of the current through them and the difference of potential at two points 4 centims. apart. As the rods are about 7·5 centims. long, and the current was introduced through a strip about 1 millim. broad, situated at the ends of the curved surfaces of the rods, the current may, to the degree of accuracy aimed at in the present paper, be assumed to be uniformly distributed throughout the cross section of the rod in the interval between the two knife edges at which the potential difference is measured.* If R_R is the resistance found, ρ the resistivity of the material, A the area of cross section of the rod, and $2a$ the distance between the knife edges, we may therefore write $\rho = R_R A/2a$.†

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* The distribution of potential v throughout a rod of length $2l$ and radius R and resistivity ρ, through which an electric current flows which enters and leaves by strips of breadth b of the curved surface at each end, and is of uniform density c at each strip, is given by the equation

$$v = \frac{8cl\rho}{\pi^2} \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n+1)^2} \sin (2n+1)\frac{\pi b}{2l} \sin (2n+1)\frac{\pi x}{2l}\, I_0\left((2n+1)\frac{\pi r}{2l}\right) \Big/ I_1\left((2n+1)\frac{\pi R}{2l}\right),$$

where x is the distance of a point from the central transverse section, r is its distance from the axis of the rod, and $I(r)$ is the Bessel function with unreal argument.

Hence the potentials at the points $\pm a$, R on the surface at which the knife edges touch the rod differ from that at the central section by

$$v_a = \frac{8cl\rho}{\pi^2} \sum_{n=0}^{\infty} (-1)^n \frac{1}{(2n+1)^2} \sin (2n+1)\frac{\pi b}{2l} \sin (2n+1)\frac{\pi a}{2l}\, I_0\left((2n+1)\frac{\pi R}{2l}\right) \Big/ I_1\left((2n+1)\frac{\pi R}{2l}\right),$$

or, if C is the total current ($= 2\pi R b c$),

$$v_a = \frac{4Cl\rho}{\pi^3 b R} \sum_{n=0} (-1)^n \frac{1}{(2n+1)^2} \sin (2n+1)\frac{\pi b}{2l} \sin (2n+1)\frac{\pi a}{2l}\, I_0\left((2n+1)\frac{\pi R}{2l}\right) \Big/ I_1\left((2n+1)\frac{\pi R}{2l}\right).$$

In the apparatus used $l = 3·75$, $a = 2$, $b = ·1$, $R = ·29$ centim.

Hence

$$\frac{\pi b}{2l} = 2°·4, \quad \frac{\pi a}{2l} = 48°, \quad \frac{\pi R}{2l} = ·121,$$

and the equation reduces to

$$v_a = \frac{C\rho a}{\pi R^2} \text{ to within 1 part in 500.}$$

The above statement is therefore correct to 1 part in 500.

† If R is the radius of the rod, and $2a$ the distance apart of the knife edges at 0° C., at any temperature θ° C. we have

$$\rho = R_R A/2a\,[1 + (2\alpha - \beta)\,\theta],$$

where α is the mean coefficient of expansion of the material of the rod, and β that of the copper frame holding it, between 0° C. and θ° C.

The values of the mean coefficients of expansion of metals at low temperatures are only known in a few cases, but from these cases it does not seem likely that the value of the correcting factor $1 + (2\alpha - \beta)\,\theta$ exceeds 1 by more than 1 part in 200, in any of the experiments.

Results of Electrical Conductivity Experiments.

The following tables of resistivities at different temperatures embody the results of the observations:—

Silver Rod.

Ag = ·999.

Density at 21° C. = 10·47.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
− 21·3	1·684 × 10^{-6}	− 109·0	0·880 × 10^{-6}
− 176·1	0·456	− 102·5	·923
− 178·1	·455	− 98·6	·942
− 178·5	·453	− 54·9	1·236
− 178·3	·472	− 52·8	1·239
− 177·9	·471	− 50·6	1·245
− 177·6	·470	− 13·0	1·468
− 177·5	·470	− 12·0	1·471
− 151·2	·609	+ 21·0	1·675
− 144·9	·660	21·0	1·676
− 139·2	·693		

Aluminium Rod.

Al = ·99.

Density at 20° C. = 2·70.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 21·1	2·97 × 10^{-6}	− 113·3	1·356 × 10^{-6}
20·7	2·97	− 108·9	1·415
− 181·5	0·623	− 103·0	1·480
− 178·3	·645	− 40·5	2·256
− 169·3	·711	− 36·0	2·301
− 162·2	·782	− 35·0	2·301
− 153·9	·885	− 33·9	2·305
− 146·6	·978	+ 12·2	2·86

Copper Rod.

Soft-drawn High-conductivity Copper.

Density at 23° C. = 8·84.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
− 176·8	0·375 × 10^{-6}	− 133·4	0·677 × 10^{-6}
− 175·7	·375	− 130·3	·707
− 173·9	·384	− 105·0	·884
− 173·0	·394	− 102·0	·909
− 172·7	·398	− 97·0	·936
− 171·1	·401	− 91·1	·989
− 159·0	·484	− 36·0	1·365
− 155·2	·508	− 32·7	1·388
− 151·2	·543	− 17·0	1·502
− 143·9	·579	− 15·5	1·506
− 141·6	·612	+ 16·9	1·753
− 136·9	·637	16·9	1·750

Zinc Rod.

Pure Redistilled.

Density at 21° C. = 7·10.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 18·8	6·30 × 10^{-6}	− 66·9	4·41 × 10^{-6}
− 180·3	1·699	− 62·9	4·46
− 179·2	1·732	− 24·7	5·36
− 174·6	1·833	− 20·3	5·48
− 171·5	1·931	− 17·6	5·52
− 168·4	1·96	+ 16·7	6·30
− 168·2	1·96	18·8	6·34
− 116·3	3·26	47·8	6·99
− 107·0	3·50	51·7	7·09
− 99·7	3·69	54·3	7·14
− 87·2	3·93	90·3	8·01
− 78·6	4·14	90·0	8·03
− 70·1	4·32	88·8	7·99

CADMIUM ROD.

Pure Redistilled.

Density at 21° C. = 8·64.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 21·0	$7 \cdot 72 \times 10^{-6}$	− 75·1	$5 \cdot 05 \times 10^{-6}$
21·0	7·72	− 70·1	5·15
− 178·1	2·22	− 65·4	5·28
− 174·1	2·34	− 59·9	5·46
− 171·0	2·41	− 32·5	6·18
− 167·9	2·48	− 29·3	6·28
− 165·9	2·56	− 25·2	6·38
− 125·4	3·67	− 23·5	6·44
− 116·9	3·87	− 5·7	6·96
− 110·5	4·07	+ 22·8	7·78
− 105·8	4·18	22·8	7·78

TIN ROD.

Pure Tin (KAHLBAUM).

Density at 21° C. = 7·28.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 11·6	$10 \cdot 65 \times 10^{-6}$	− 98·6	$5 \cdot 96 \times 10^{-6}$
− 170·4	3·00	− 91·3	6·24
− 170·4	3·00	− 87·7	6·44
− 169·1	3·17	− 52·9	7·88
− 165·9	3·26	− 48·8	8·08
− 164·7	3·36	− 46·7	8·13
− 162·3	3·42	− 42·2	8·29
− 163·1	3·45	− 40·0	8·42
− 150·8	3·51	− 36·1	8·59
− 148·8	3·96	+ 11·8	10·70
− 107·0	5·58	13·3	10·75
− 103·1	5·77	13·3	10·75

BRASS ROD.

Approx. ·70 Cu, ·30 Zn.

Density at 22° C. = 8·44.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 21·5	$6 \cdot 57 \times 10^{-6}$	− 92·3	$5 \cdot 06 \times 10^{-6}$
21·4	6·57	− 87·2	5·13
− 174·5	3·84	− 78·6	5·20
− 171·0	3·89	− 76·6	5·23
− 165·1	3·97	− 68·8	5·34
− 161·2	4·03	− 29·3	5·89
− 158·9	4·09	− 25·7	5·93
− 150·8	4·16	− 22·7	5·98
− 109·1	4·78	− 20·4	6·02
− 104·6	4·84	+ 14·9	6·50
− 99·5	4·94		

IRON ROD.

Fe = ·994.

Density at 21° C. = 7·74.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 19·9	$14 \cdot 33 \times 10^{-6}$	− 81·8	$8 \cdot 98 \times 10^{-6}$
− 175·3	4·90	− 77·6	9·15
− 175·8	4·87	− 71·4	9·48
− 175·5	4·86	− 69·5	9·56
− 175·6	4·86	− 66·9	9·67
− 174·2	4·89	− 61·4	9·96
− 170·3	5·01	− 21·8	12·03
− 166·3	5·20	− 19·2	12·19
− 159·4	5·45	− 16·1	12·33
− 154·4	5·64	− 14·0	12·46
− 129·6	6·76	+ 10·3	13·70
− 121·4	7·08	22·1	14·46
− 117·0	7·34	21·0	14·30
− 111·1	7·59	18·3	14·21
− 106·7	7·81	16·7	14·16
− 99·7	8·16		

Nickel Rod.

Ni = ·99.

Density at 21° C. = 8·80.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 17·7	$12·87 \times 10^{-6}$	− 70·3	$9·04 \times 10^{-6}$
− 178·1	5·42	− 65·0	9·29
− 178·7	5·41	− 60·6	9·48
− 181·7	5·29	− 50·0	9·92
− 158·6	5·92	− 41·3	10·26
− 147·3	6·24	− 39·8	10·36
− 137·1	6·61	− 34·5	10·61
− 117·5	7·22	− 28·3	10·86
− 107·8	7·76	− 24·1	11·02
− 101·8	7·94	+ 19·3	12·92
− 94·3	8·24	22·1	13·05
− 88·4	8·42	22·1	13·07
− 79·8	8·74		

Lead Rod.

Pure.

Density at 25° C. = 11·29.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 17·4	$20·9 \times 10^{-6}$	− 92·2	$12·7 + 10^{-6}$
17·2	20·9	− 89·2	12·9
− 167·2	6·98	− 55·4	15·3
− 170·0	6·71	− 53·7	15·5
− 137·7	9·01	− 53·0	15·6
− 135·7	9·25	− 51·8	15·7
− 132·7	9·45	− 14·5	18·5
− 129·4	9·71	− 14·0	18·5
− 96·0	12·3	+ 15·7	20·8
− 94·6	12·6		

Steel Rod.

C approx. ·01.

Density at 24° C. = 7·84.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 16·2	$18·33 \times 10^{-6}$	− 101·9	$11·13 \times 10^{-6}$
− 172·7	7·19	− 95·8	11·49
− 173·9	7·12	− 92·7	11·69
− 172·2	7·18	− 40·8	14·74
− 165·2	7·54	− 39·6	14·84
− 154·8	8·07	− 36·0	15·08
− 146·9	8·36	+ 21·8	18·67
− 111·0	10·53	22·1	18·71

Platinoid Rod.

Approx. ·62 Cu, ·15 Ni, ·22 Zn.

Density at 22° C. = 8·66.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 21·2	$34·4 \times 10^{-6}$	− 99·5	$33·1 \times 10^{-6}$
− 171·0	32·4	− 96·4	33·1
− 173·0	32·3	− 92·1	33·3
− 172·0	32·4	− 71·0	33·3
− 160·2	32·3	− 66·6	33·5
− 155·0	32·4	− 35·0	33·7
− 146·7	32·6	− 24·4	33·8
− 134·6	32·8	+ 10·0	34·3
− 103·9	33·0	10·5	34·3

German Silver Rod.

Approx. ·62 Cu., ·15 Ni, ·22 Zn.

Density at 22° C. = 8·67.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 17·2	39·9 × 10^{-6}	− 116·1	38·3 × 10^{-6}
17·2	39·8	− 105·3	38·4
− 169·1	38·0	− 95·5	38·6
− 168·2	38·0	− 57·2	39·0
− 167·7	38·0	− 53·3	39·1
− 159·3	38·0	− 50·9	39·1
− 153·0	37·9	− 16·5	39·5
− 145·8	37·9	− 15·5	39·5
− 134·6	38·0	+ 16·7	39·8
− 126·9	38·1	16·3	39·8

Manganine Rod.

Approx. ·84 Cu, ·04 Ni, ·12 Mn.

Density at 22° C. = 8·42.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 17·7	44·6 × 10^{-6}	− 66·8	44·4 × 10^{-6}
17·7	44·6	− 51·8	44·5
− 161·0	43·3	− 50·2	44·5
− 164·0	43·0	− 46·3	44·5
− 163·5	43·0	− 43·6	44·5
− 163·0	43·0	− 26·0	44·5
− 154·5	43·1	− 17·5	44·5
− 145·3	43·2	− 14·0	44·5
− 133·6	43·4	− 13·5	44·5
− 119·2	43·9	+ 13·6	44·5
− 109·9	44·0	13·8	44·5
− 98·5	44·2		

Lipowitz Alloy Rod.

Approx. ·50 Bi, ·25 Pb, ·14 Sn, ·11 Cd.

Density at 20° C. = 9·66.

Temp., H. scale.	Resistivity, ohm per centim. cube.	Temp., H. scale.	Resistivity, ohm per centim. cube.
° C.		° C.	
+ 19·6	47·5 × 10^{-6}	− 122·9	28·9 × 10^{-6}
− 176·6	21·3	− 92·1	33·2
− 178·1	21·1	− 89·1	33·7
− 178·5	21·0	− 87·0	34·0
− 178·5	20·9	− 85·1	34·3
− 175·7	21·0	− 37·4	40·4
− 173·4	21·5	− 35·7	40·9
− 170·5	21·8	− 35·0	41·0
− 141·5	26·1	− 34·6	41·0
− 134·6	27·4	+ 12·1	46·7
− 129·3	27·9	12·1	46·8
− 125·4	28·3		

The results given in the foregoing tables are shown graphically in Plate 30, in which the crosses indicate values obtained by observation. To get a more compact diagram the scale has been varied to suit the substances tested, and the words which follow the names of the substances on the diagram, *e.g.*, "1/10 scale," indicate that the values plotted in the diagram are that particular fraction of *e.g.*, 1/10 of the values observed.

The values found by JÄGER and DIESSELHORST at 18° C. and 100° C. are shown by the broken lines to the right. The lines for the same material in the two cases are joined by a dotted line or by a bracket.

As the electrical resistivity of a metal is nearly proportional to the absolute temperature, *i.e.*, the electrical conductivity multiplied by the absolute temperature nearly a constant, and as this product is required in the discussion which follows, a table of values of the quantity at a number of temperatures within the range covered by the experiments is given on p. 437. It has been calculated from the values of the resistances taken from the curves of Plate 30.

Discussion of the Electrical Results.

A comparison of the values of the electrical resistivities obtained in the present experiments with those obtained at 18° C. and 100° C. by JÄGER and DIESSELHORST, shows that the agreement is not quite so good as in the case of the thermal measurements. This is not likely to be due to errors of observation, as the electrical measurements admit of greater accuracy than the thermal. It seems rather to point to the greater influence on the electrical properties than on the thermal, of small differences in chemical composition, or in physical structure. This is in keeping with the results obtained by GRÜNEISEN* in the cases of copper and iron.

The influence of impurity on the electrical resistivities of metals is, in fact, so marked, particularly at low temperatures,† that a comparison of the resistivities found in the present experiments with those found by DEWAR and FLEMING (D.F.), and by KAMERLINGH ONNES and CLAY (O.C.), will serve as a test of the degree of purity of the materials used.

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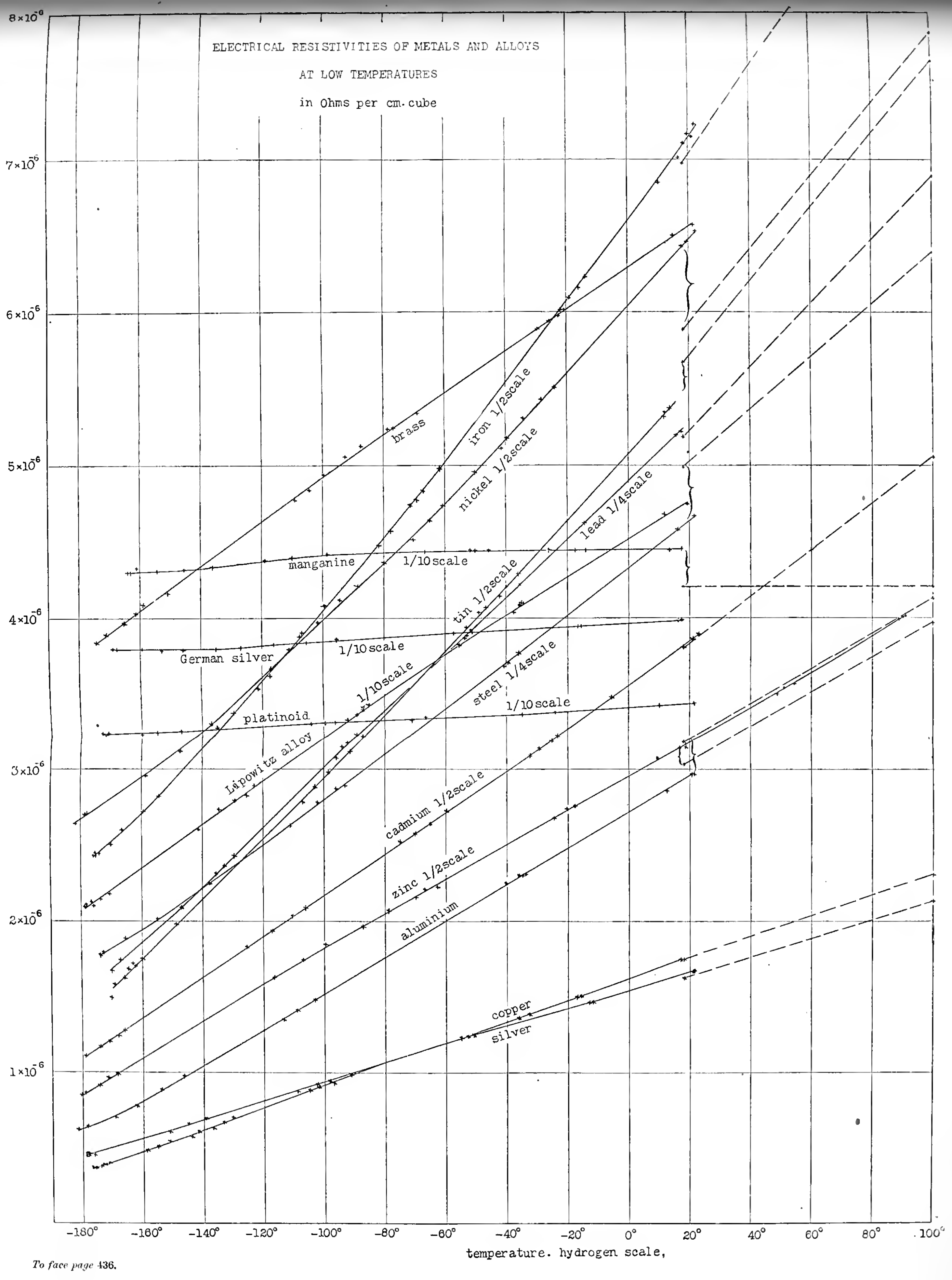
* GRÜNEISEN, 'Ann. der Phys.,' 3, p. 43 (1900).

† MATTHIESSEN, 'Ann. der Phys.,' 122, pp. 19, 68 (1864). DEWAR and FLEMING, 'Phil. Mag.,' 36, p. 271, (1893); FLEMING, 'Proc. Roy. Inst.,' June, 1896, p. 9. KAMERLINGH ONNES and CLAY, 'Comm. Leiden,' No. 99^c (1907).



To face page 436.

TABLE of Values of Electrical Conductivity Multiplied by Absolute Temperature for Metals and Alloys.

Conductivities in Reciprocal Ohms per Centimetre Cube.

Temperatures on Hydrogen Scale.

Temperatures . . .	– 170° C.	– 160° C.	– 150° C.	– 125° C.	– 100° C.	– 75° C.	– 50° C.	– 25° C.	0° C.	+ 18° C.
Copper	251	230	224	202	188	180	175	172	169	165 × 10^6
Silver	204	200	197	188	184	180	177	178	176	175
Zinc	53·2	51·5	50·5	48·5	47·6	46·9	46·7	46·3	46·1	46·1
Cadmium	42·2	41·5	41·2	40·5	39·8	39·4	39·1	38·8	38·3	38·0
Aluminium . . .	147	139	132	121	114	109	105	102	100	99
Tin	33·0	32·3	31·3	30·3	29·3	28·7	27·9	27·4	26·9	26·6
Lead	15·3	15·2	15·1	14·7	14·3	14·2	14·1	14·0	13·9	13·9
Iron	20·4	20·9	21·1	21·3	21·4	21·3	21·1	20·9	20·7	20·6
Nickel	18·3	19·2	20·0	21·1	21·7	22·2	22·5	22·6	22·6	22·6
Steel	14·1	14·5	14·8	15·2	15·5	15·6	15·7	15·7	15·8	15·8
Brass	26·4	27·9	29·4	32·5	35·1	37·6	39·8	41·7	43·5	44·4
German silver . .	2·70	2·98	3·24	3·88	4·50	5·10	5·71	6·29	6·90	7·30
Platinoid	3·17	3·48	3·77	4·50	5·24	5·95	6·67	7·35	8·00	8·47
Manganine . . .	2·39	2·62	2·85	3·39	3·92	4·46	5·03	5·59	6·13	6·54
Lipowitz alloy . .	4·65	4·81	4·93	5·18	5·38	5·56	5·75	5·92	6·02	6·13

TABLE of Electrical Resistivities, and of the Ratio of Resistivities at −170° C. and at 0° C.

ρ in ohms per centimetre cube.

	ρ_0.	ρ_{-170}/ρ_0.		ρ_0.	ρ_{-170}/ρ_0.
Copper . . .	1·62 × 10^{-6}	·253	Tin	10·16 × 10^{-6}	·307
	1·56	·241 D.F.		13·1	·310 D.F.
	1·58	N.*	Lead. . . .	19·6	·345
Silver	1·55	·326		20·4	·343 D.F.
	1·49	·317 D.F.		—	·345 O.C.
	—	·305 O.C.		19·8	N.
	1·51	N.	Iron	13·16	·383
Aluminium . .	2·72	·257		9·11	·188 D.F.
	2·58	·272 D.F.		10·7	N.
	2·62	N.	Nickel . . .	12·08	·465
Zinc	5·92	·328		12·35	·207 D.F.
	5·77	·312 D.F.		12·0	N.
Cadmium . .	7·12	·343			
	10·0	·343 D.F.			

The values of the ratio ρ_{-170}/ρ_0 in the case of DEWAR and FLEMING'S metals have been calculated from their tables of results with the help of CALLENDAR'S table,[†] connecting their platinum temperatures with hydrogen temperatures.

From this table it follows on the strength of MATTHIESSEN'S rule that impurity raises the resistivity, that the materials used in the present experiments were, in some cases less and in some cases more pure than those used by DEWAR and FLEMING. In most cases the difference is not large, but in the cases of cadmium and tin the materials used have a considerably less resistivity, and in the case of iron a considerably greater resistivity than those used by DEWAR and FLEMING. In the case of nickel and iron the ratios of the resistivity at −170° C. to that at 0° C., are much larger than the corresponding ratios calculated from their observations. The total amount of impurity present in each of these specimens is less than 1 per cent., so that the influence of even small quantities of impurity seems to be very marked.

The table of values of the product of electrical conductivity into absolute temperature, given on p. 437, shows a general tendency for the product to increase with decrease of temperature for all the metals tested except iron and nickel, and these contained a little impurity. The increase is relatively small in the case of lead,

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[*] NICCOLAI'S results, 'Accad. Lincei Atti,' 16, p. 906 (1907). His results at low temperatures have not been used, as there is no indication that the temperature readings of the thermo-junctions used by him have been reduced to the hydrogen scale.

[†] CALLENDAR, 'Phil. Mag.,' 47, p. 214 (1899).

which, however, was very free from impurity. All the alloys show a decrease of the product as the temperature decreases.

A comparison of this table with the table of thermal conductivities given on p. 426 will show that there is some similarity between the two.

SECTION III.—COMPARISON OF THERMAL AND ELECTRICAL CONDUCTIVITIES.

In 1882 L. LORENZ[*] showed by measuring both the thermal and electrical conductivities of bars of a number of different metals, that the quotient of the thermal by the electrical conductivity was not constant, as WIEDEMANN and FRANZ[†] had supposed, but increased with the temperature, so as to be nearly proportional to the absolute temperature, a result which he had anticipated[‡] on theoretical grounds. His results did not attract much attention till the publication of RIECKE'S electron theory of conduction in 1898[§] and the confirmation of LORENZ'S theory for pure metals between the temperatures 18° C. and 100° C. by JÄGER and DIESSELHORST, in 1899,[||] by a method which gives the quotient of the two conductivities directly.

Next year DRUDE'S electron theory appeared,[¶] and more recently H. A. LORENTZ has published one.[**]

According to these theories the electricity and energy are supposed to be carried entirely by free electrons which move to and fro and come into collision with the molecules of the metal and with each other, and are assumed to have on the average the same kinetic energy of translation as the molecules of a gas at the same temperature. In the first two theories both positive and negative electrons are movable, in the third the negative only.

On the former theories if we limit ourselves to two kinds of electrons carrying charges e_1 and e_2 where $e_2 = -e_1 = -e$, and if n_1, n_2 are the numbers per cubic centimetre, u_1, u_2 their velocities at a temperature t, l_1, l_2 their mean free paths, we have the thermal conductivity

$$k = \tfrac{1}{3}\alpha\,(n_1u_1l_1+n_2u_2l_2),$$

and the electrical conductivity

$$\kappa = (\alpha t)^{-1}\,(n_1u_1l_1e_1^{\,2}+n_2u_2l_2e_2^{\,2}),$$

where α is the mean kinetic energy of translation of a gas molecule at absolute temperature 1°.

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[*] L. LORENZ, 'Ann. der Phys.,' 13, p. 422 (1882).

[†] G. WIEDEMANN and R. FRANZ, 'Ann. der Phys.,' 89, p. 497 (1853).

[‡] L. LORENZ, 'Ann. der Phys.,' 147, p. 429 (1872).

[§] E. RIECKE, 'Ann. der Phys.,' 66, p. 353 and 545 (1898).

[||] W. JÄGER and H. DIESSELHORST, 'Sitz.-Ber. Akad. Wiss. Berlin,' 38, p. 719 (1899); and 'Abhand. der Phys.-Tech. Reichsanstalt,' 3, p. 282 (1900).

[¶] P. DRUDE, 'Ann. der Phys.,' 1, p. 566, 3, p. 369 (1900).

[**] H. A. LORENTZ, 'Proc. Amsterdam,' 7, p. 438, &c. (1905).

Hence

$$k/\kappa t = \tfrac{4}{3}\,(\alpha/e)^2.$$

The value of e, the charge on an electron, is known with a fair degree of accuracy to be $1{\cdot}1 \times 10^{-20}$ electromagnetic units,[*] but the value of α is still uncertain, as it depends on the number n of molecules in a cubic centimetre of a gas ($\alpha = 3\,.\,\text{pressure}/2n$ abs. temp.). The following table gives a few of the values which have been found for n by various methods and the values of α and of $k/\kappa t$ calculated from them :—

Author.	Method.	n.	α.	$k/\kappa t$.
Kelvin[†]	Viscosity of gas and density when condensed	1×10^{20}	$5{\cdot}6 \times 10^{-17}$	$3{\cdot}3 \times 10^{-9}$
Kelvin[‡]	Effect of atmosphere on light . .	$>2{\cdot}4 \times 10^{19}$	$<2{\cdot}3 \times 10^{-16}$	$<5{\cdot}9 \times 10^{-8}$
Jeans[§]	Viscosity of gas and Van der Waals' b	$4{\cdot}6 \times 10^{19}$	$1{\cdot}2 \times 10^{-16}$	$1{\cdot}6 \times 10^{-8}$
Planck[‖]	Radiation theory and entropy . .	$2{\cdot}8 \times 10^{19}$	$2{\cdot}0 \times 10^{-16}$	$4{\cdot}3 \times 10^{-8}$
Lorentz[¶] . . .	Radiation theory	—	$1{\cdot}2 \times 10^{-16}$	$1{\cdot}6 \times 10^{-8}$
J. J. Thomson[**] H. A. Wilson[††]	Determination of e and assumption that atom of H in electrolysis carries charge e .	4×10^{19}	$1{\cdot}4 \times 10^{-16}$	$2{\cdot}2 \times 10^{-8}$
	[‡‡] Ditto, but assuming charge on H atom to be $2e$	2×10^{19}	$2{\cdot}8 \times 10^{-16}$	$8{\cdot}7 \times 10^{-8}$

From this it appears that we are not yet in a position to calculate more than the order of magnitude of the constant $\frac{4}{3}(\alpha/e)^2$ which the electronic theories give as the value of $k/\kappa t$.

In order to see how far the theoretical result agrees in other respects with the observed facts, the values of $k/\kappa t$ at various temperatures for the metals and alloys tested have been calculated from the values of the thermal and electric conductivities given in the tables on pp. 426 and 437. The results are shown in the following table and in the curves on Plate 31.

The corresponding values calculated from Jäger and Diesselhorst's experiments at 18° C. and 100° C. are also given for comparison.

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[*] The mean of J. S. Townsend's ('Phil. Mag.,' 45, p. 133 (1898)), J. J. Thomson's ('Phil. Mag.,' V., p. 355 (1903)), and H. A. Wilson's results ('Phil. Mag.,' V., p. 441 (1903)).

[†] Kelvin, 'Phil. Mag.,' 4, p. 197 (1902).

[‡] Kelvin, 'Phil. Mag.,' 4, p. 301 (1902).

[§] J. H. Jeans, 'Phil. Mag.,' 8, p. 694 (1904).

[‖] M. Planck, 'Ann. der Phys.,' 4, p. 566 (1901).

[¶] H. A. Lorentz, 'Versl. Akad. van Wet.,' 14, p. 518, &c. (1906).

[**] J. J. Thomson, 'Phil. Mag.,' 5, p. 355 (1903).

[††] H. A. Wilson, 'Phil. Mag.,' 5, p. 441 (1903).

[‡‡] This line is added since Professor Townsend's proof that when a gas is ionised by Röntgen rays there are only half so many positive as negative ions produced ('Proc. Roy. Soc.,' 80, p. 210, 1908), seems to render it advisable to take into account the possibility of the H atom in electrolysis having a charge $2e$.

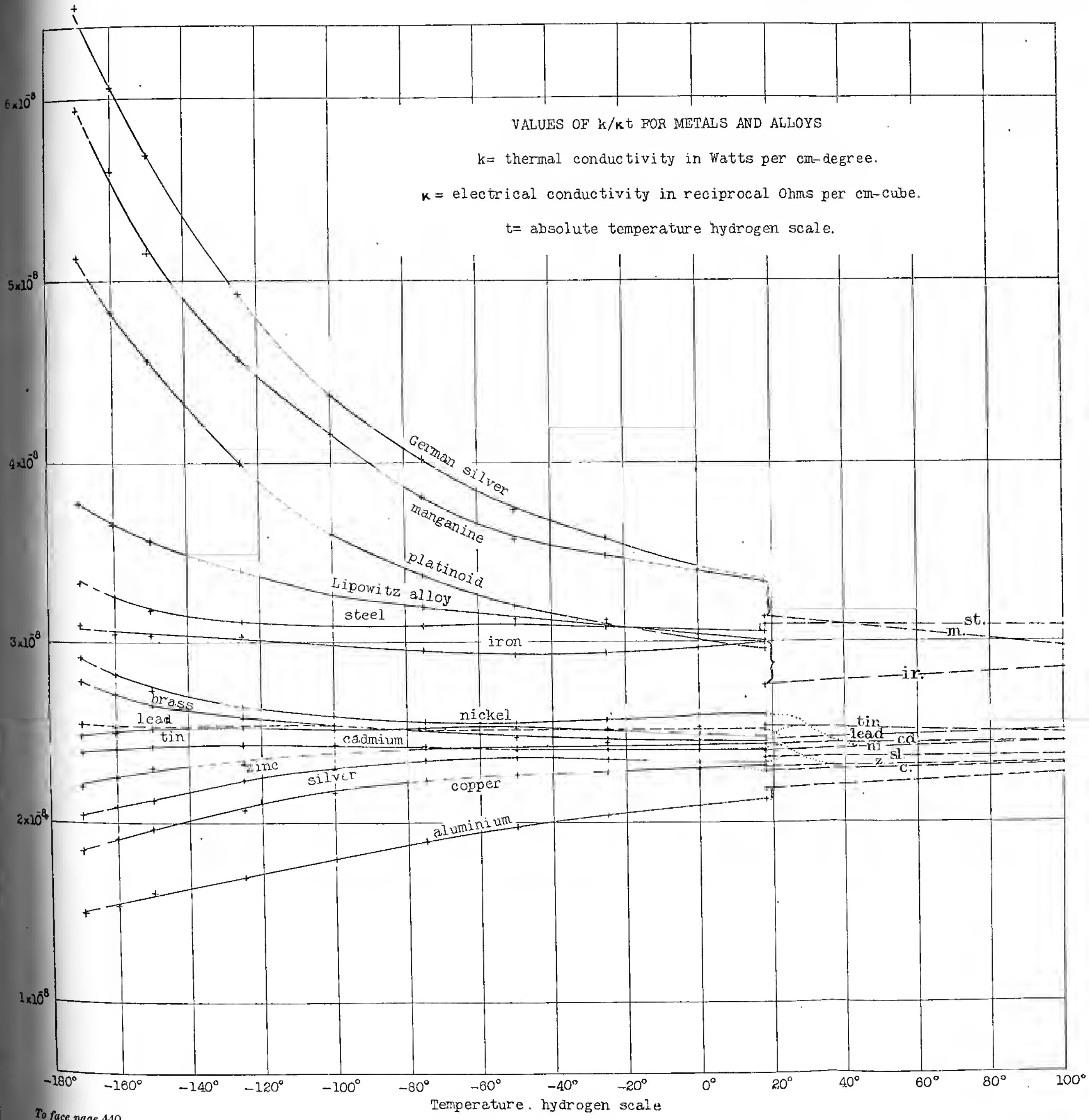
VALUES OF k/κt FOR METALS AND ALLOYS
k= thermal conductivity in Watts per cm-degree.
κ = electrical conductivity in reciprocal Ohms per cm-cube.
t= absolute temperature hydrogen scale.
6×10⁻⁸
5×10⁻⁸
4×10⁻⁸
3×10⁻⁸
2×10⁻⁸
1×10⁻⁸
German silver
manganine
platinoid
Lipowitz alloy
steel
iron
brass
lead
tin
nickel
cadmium
zinc
silver
copper
aluminium
st.
m.
ir.
tin
lead
cd
ni
sl
z
c.
−180°
−160°
−140°
−120°
−100°
−80°
−60°
−40°
−20°
0°
20°
40°
60°
80°
100°
Temperature. hydrogen scale

TABLE of Values of $k/\kappa t$ Calculated from the Present Experiments Compared with those Calculated from JÄGER and DIESSELHORST'S Results.

k, the thermal conductivity in watts per centimetre-degree.
κ, the electrical conductivity in reciprocal ohms per centimetre cube.
t, absolute temperature on the hydrogen scale.

	From the present experiments.										From JÄGER and DIESSELHORST'S experiments.	
Temperatures . . .	− 170° C.	− 160° C.	− 150° C.	− 125° C.	− 100° C.	− 75° C.	− 50° C.	− 25° C.	0° C.	+ 18° C.	18° C.	100° C.
Aluminium	1·50	1·54	1·61	1·70	1·81	1·90	1·98	2·04	2·09	2·13	2·19	2·27 × 10^{-8}
Copper	1·85	1·92	1·97	2·07	2·17	2·23	2·26	2·28	2·30	2·32	2·29	2·32
Silver	2·04	2·09	2·13	2·24	2·29	2·34	2·36	2·35	2·33	2·33	2·36	2·37
Zinc	2·20	2·25	2·30	2·33	2·39	2·41	2·40	2·44	2·45	2·43	2·31	2·33
Cadmium	2·39	2·41	2·42	2·43	2·43	2·42	2·41	2·40	2·40	2·39	2·43	2·44
Tin	2·48	2·49	2·53	2·52	2·51	2·52	2·53	2·51	2·49	2·47	2·53	2·49
Lead*	2·55	2·53	2·52	2·54	2·54	2·51	2·52	2·51	2·53	2·51	2·46	2·51
Nickel	2·92	2·82	2·73	2·63	2·59	2·56	2·55	2·57	2·59	2·59	2·40	2·44
Iron	3·10	3·05	3·04	3·03	2·98	2·95	2·93	2·94	2·97	2·99	2·76	2·85
Steel	3·34	3·26	3·19	3·11	3·09	3·09	3·10	3·09	3·06	3·05	3·10	3·09
Brass	2·78	2·71	2·65	2·57	2·54	2·51	2·47	2·46	2·45	2·45		
Lipowitz alloy . . .	3·78	3·66	3·57	3·40	3·27	3·20	3·13	3·11	3·05	3·00		
Platinoid	5·13	4·82	4·56	4·00	3·61	3·38	3·21	3·13	3·01	2·96		
Manganine	5·94	5·60	5·16	4·57	4·16	3·81	3·58	3·49	3·41	3·34	3·14	2·97
German silver . . .	6·51	6·06	5·69	4·93	4·37	4·02	3·75	3·59	3·41	3·36		

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* MACHIA, 'Acc. Lincei Atti,' 16, p. 507 (1907), finds a rather greater increase of the conductivity constant for lead at low temperatures.

The curves show that there is a tendency for the values of the conductivity constant $k/\kappa t$ to collect in the neighbourhood of the value $2{\cdot}4 \times 10^{-8}$, within the range given by the electronic theories, and that this tendency is rather more marked in the values calculated from JÄGER and DIESSELHORST'S results than in those calculated from the present experiments. Lead, tin, and possibly cadmium give values independent of temperature over the wide range covered, and therefore support the statement made by L. LORENZ in 1882. Zinc, silver, copper and aluminium show a marked decrease of the constant as the temperature decreases. Nickel, steel, and possibly iron, show an increase as the temperature decreases. This appears to be the characteristic behaviour of alloys. The values for aluminium and copper are decidedly below, while those for nickel and iron are decidedly above. the value 2·4. All the alloys give values above this, and, with the exception of brass, decidedly above. This large value of the constant for alloys especially at low temperatures is in keeping with and extends the results obtained previously by GRÜNEISEN,* who found that increase of impurity in copper and iron at ordinary temperatures increased the value of the constant.

It is necessary to bear this increase in mind in basing any argument on the values observed. The high values for nickel and iron may, since both contained a little impurity (about 1 per cent.), be ascribed to the impurity. In the cases of the other metals, with the exception of aluminium, which contained a little impurity (about 1 per cent.), it is not probable that any small amount of impurity present in them could have materially influenced the positions of the curves. In the case of aluminium it seems possible that the curve at low temperatures may be a little high, owing to the small quantity of impurity present in the metal.

The only conclusion which can be drawn from the curves seems to be that the Lorenz law of constancy of the value of $k/\kappa t$ at different temperatures for each metal has only a restricted application, and that although the metals which support the law give nearly the same value, 2·4, for the constant,† the other metals have values of the constant which differ from 2·4 by amounts far outside the limits of experimental error.‡

These facts are not of such a character as to provide strong support for any of the electronic theories mentioned on p. 439 in their present forms.

A modified theory has been put forward recently by Professor J. J. THOMSON§ to get over a difficulty he pointed out in the older theories, which made the energy

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* E. GRÜNEISEN, 'Ann. der Phys.,' 3, p. 43 (1900).

† It is worthy of note that for mixtures of these metals, MATTHIESSEN, 'Ann. der Phys.,' 110, p. 190 (1860), found that the electrical conductivities, and SCHULZE, 'Ann. der Phys.,' 9, p. 555 (1902), that the thermal conductivities, could be calculated from the relative volumes of the constituents present.

[‡ *Note added June* 1.—The variations of the values of $k/\kappa t$ for the same metals at higher temperatures will form the subject of a future communication.]

§ J. J. THOMSON, 'Journ. Inst. Elect. Eng.,' 38, p. 455 (1907), or 'Corpuscular Theory of Matter,' p. 86.

absorbed by the electrons in 1 gramme of a metal during an increase of temperature of 1° C. far exceed the observed specific heat of the metal. In this theory the electrons pass from one doublet, consisting of a positively and negatively charged atom, to another similar doublet, which have arranged themselves along the line of electric force, as in the old theory of electrolysis the molecules of the Grotthus chains were supposed to do. If d is the distance apart of the charges of the doublet, and b is the distance between the doublets, THOMSON shows that $k/\kappa t$ is $9b/8a$ times the value found on the former theory. Since b/a may vary in value from metal to metal, and in the same metal at different temperatures, this theory may by a proper choice of the laws of variation be brought into unison with the observed facts.

It is, however, open to doubt whether any theory which does not take into account the atomic differences of the various metals can give a satisfactory explanation of the whole facts. The nearness to each other of the curves for metals belonging to the same chemical group, Plate 31, suggests that atomic properties play their part in determining the behaviour of a metal to the flow of heat and electricity through it.

Electronic theories have regarded the free electrons as the sole carriers of energy from molecule to molecule, and have therefore been unable to deal with the thermal conductivities of electrical insulators, in which there can be no free electrons. Now the thermal conductivities of some substances which insulate electrically are as large as those of the worse conducting metals, *e.g.*, the thermal conductivity of quartz along the axis is 0·029, while that of bismuth is only 0·016 to 0·019. It seems, therefore, that a theory of heat conduction which ascribes it to free electrons alone must be a very partial account of it.

The fact pointed out on p. 427, that the variation of the thermal conductivities of the metals with temperature is of the same character as, though less marked than, the corresponding variations for electrical insulators, and that alloys vary in a manner similar to the only mixture (glass) of insulators yet investigated, both support this contention, that theories which depend solely on free electrons as carriers can hardly claim to be adequate expressions of the phenomena.

This investigation was commenced in Manchester, where a liquid air plant was available. I have to thank Dr. E. C. C. BAILY and the authorities of University College for kindly providing me with liquid air in London.

I have also to thank the Committee administering the Government Grant for Scientific Investigations for a large proportion of the funds out of which the materials used in the investigation have been purchased.

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THE SUPERSATURATION AND NUCLEAR CONDENSATION OF CERTAIN ORGANIC VAPOURS

BY

T. H. LABY, B.A.,
EMMANUEL COLLEGE, CAMBRIDGE, EXHIBITION OF 1851 SCHOLAR OF THE UNIVERSITY OF SYDNEY, JOULE STUDENT OF THE ROYAL SOCIETY.

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XII. *The Supersaturation and Nuclear Condensation of Certain Organic Vapours.*

By T. H. LABY, *B.A., Emmanuel College, Cambridge, Exhibition of 1851 Scholar of the University of Sydney, Joule Student of the Royal Society.*

Communicated by Professor J. J. THOMSON, *F.R.S.*

Received April 10,—Read April 30, 1908.

Condensation in Water Vapour.

THE first precise measurements of the conditions causing condensation when dust-free air saturated with water vapour is expanded were made by C. T. R. WILSON.*

He calculated the cooling due to the adiabatic expansion, and then the supersaturation, which is the ratio of the actual pressure of the water vapour at the end of the expansion to the saturated vapour pressure of water at the temperature at the end of the expansion.

Mr. WILSON obtained the results given in the following table, in which v_2/v_1 is the ratio of the initial to the final gas pressure in the expansion apparatus :—

Gas.	Rain-like condensation.		Cloud-like condensation.	
	Expansion v_2/v_1.	Supersaturation.	Expansion.	Supersaturation.
Air	1·252	4·2	1·38 } 1·375	7·9
Oxygen	1·257	4·3	1·383	
Nitrogen	1·262	4·4	1·38	
Hydrogen	—	—	1·38	
Carbon dioxide . .	1·365	4·2	1·535	7·3
Chlorine	1·3	3·4	1·45	(5·9)

It was concluded from the size and number of the nuclei producing the cloud-like condensation that they were small aggregates of water molecules.

---

* 'Phil. Trans.,' A, 189, p. 265 (1897).

24.8.08

With a large apparatus (with working parts of brass) WILSON[*] some time later showed, in the absence of (artificial) external ionising rays and of an electric field, that rain-like condensation took place in air saturated with water vapour at an expansion of 1·247, while with an electric field no drops were produced even by an expansion of 1·27. Thus the natural ions act as condensation nuclei for expansions of 1·25. The number of natural ions per cubic centimetre deduced from the number of drops is in agreement with the number obtained by other methods.

The simplest interpretation of WILSON'S experiments is that there are three kinds of nuclei concerned in condensation. Nuclei of one kind are naturally present in dust-free air, oxygen, nitrogen (hydrogen ?), carbon dioxide, and chlorine; they are increased in numbers by Röntgen and Becquerel rays, ultra-violet light acting on a negatively charged zinc plate, and they are electrically charged and produce condensation in water vapour when it is supersaturated at least 4·3 times; in short, these nuclei are ions. Another type of nuclei are uncharged and are possibly aggregates of water molecules, as mentioned above. A third kind are present near the surface of zinc, lead, and amalgamated zinc plates, are uncharged, and act as nuclei when the supersaturation is not less than 4·3.

The Comparative Efficiency of Positive and Negative Ions.

WILSON[†] showed in 1899, using air and water vapour, that the negative ions are more efficient in producing condensation than the positive, for he found that expansions greater than 1·247 caught the negative ions, while both the positive and negative were caught by expansions greater than 1·31. It is to be noticed that the second point (1·31) cannot be determined as readily or with the same accuracy as the first one (1·247).

Previous Work on Organic Vapours.—F. G. DONNAN[‡] determined the expansion necessary to produce rain-like condensation, and a fog in dust-free air, saturated with the vapours of some carefully purified organic liquids.

K. PRZIBRAM[§] has made observations on the condensation of organic vapours in ionised air. He has followed WILSON in carrying out his experiments. The piston of his expansion apparatus worked in paraffin oil, which would seem undesirable when using vapours soluble in that oil.

Experimental: The Expansion Apparatus.

Two modifications of the expansion apparatus have been tried. It was not easy to

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[*] 'Phil. Mag.,' June, 1904, p. 681.

[†] 'Phil. Trans.,' A, 193, pp. 289–308 (1900).

[‡] 'Phil. Mag.,' March, 1902, p. 305.

[§] 'Sitzungsber. d. kais. Akad. d. Wissen. in Wien,' Math.-naturw. Kl., Band 115 (1906).

obtain a durable piston for expansions up to $v_2/v_1 = 2$. The expansion apparatus as used is drawn in fig. 1.

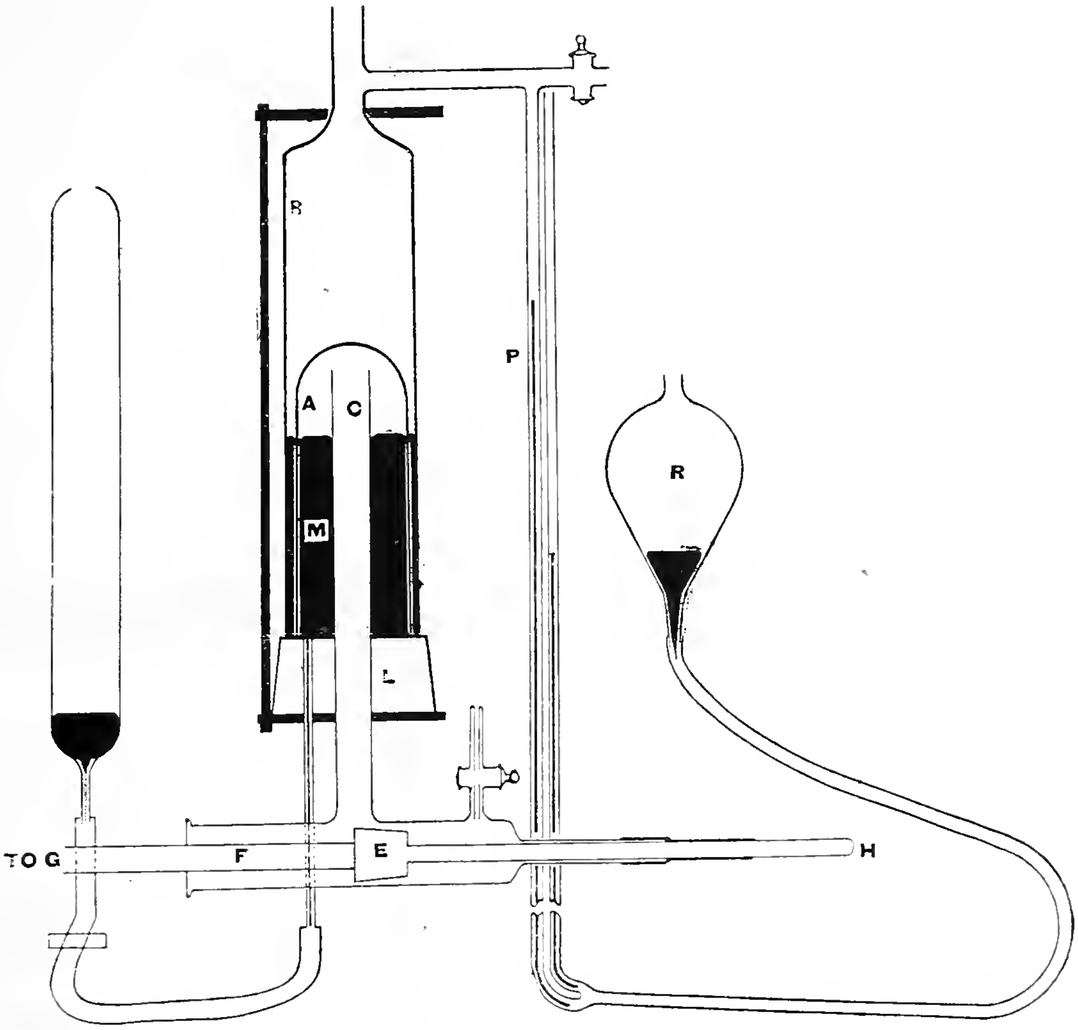

Fig. 1.

The glass piston A slides freely in B. By pulling the glass rod H, the rubber bung E is withdrawn from the mouth of the tube F, the air inside A flows suddenly into an exhausted globe G, the piston descends rapidly through the mercury M, and is suddenly brought to rest by the rubber bung L. Its ground edge remains in tight contact with the rubber, and so no mercury or gas escapes from B. As the action of the piston is very regular, as shown by the constant pressure after expansions, its dimensions may be worth mentioning. They are: height 13·2 cms., diameter 4·5 cms., weight 42 grammes. P is a mercury pressure gauge in communication with B. The reservoir is for emptying and adjusting the height of the mercury in B. This form of apparatus can be readily taken to pieces and cleaned, which was often necessary, since a number of liquids were used.

To obtain a given expansion, the piston A was adjusted in position until the initial pressure was the necessary one for that expansion.

The pressure in the 25-litre globe G, with which the tube F communicates, was kept below 80 mm. of mercury. With this pressure the piston falls rapidly—so rapidly, in fact, that a number of pistons were broken.

The amount of the expansion in any experiment is measured by

$$\frac{v_2}{v_1} = \frac{\text{the initial gas pressure}}{\text{the final gas pressure}} = \frac{B - \pi - s_1}{B - \pi - s_2},$$

where B is the barometric pressure, π the saturated vapour pressure of the liquid at the temperature of the experiment (*i.e.*, initially), and s_1 the initial and s_2 the final reading of the gauge P.

The Expansion Chambers.

The expansion chamber, used to find the least expansion to produce condensation in dust-free air saturated with the various organic vapours, is drawn in fig. 2. It was made so that only mercury and glass come in contact with the vapour. The test-tube T is fitted by the rubber cork R to the expansion apparatus E. Mercury and then the liquid to be used are admitted from M, until the liquid, which is always above the mercury, overflows into E and the lower part of the apparatus. When the apparatus is in use, the liquid L under examination lies above the mercury, as

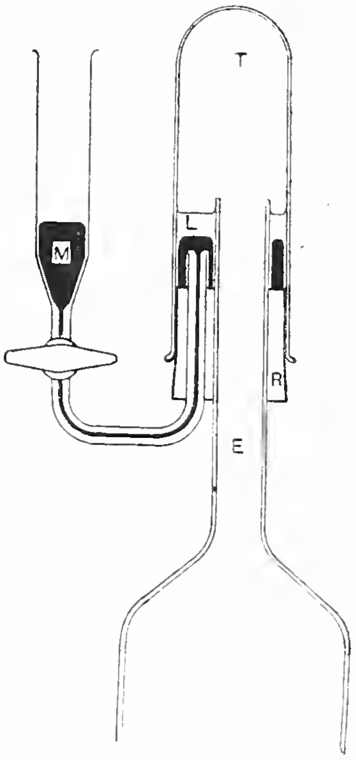

Fig. 2.

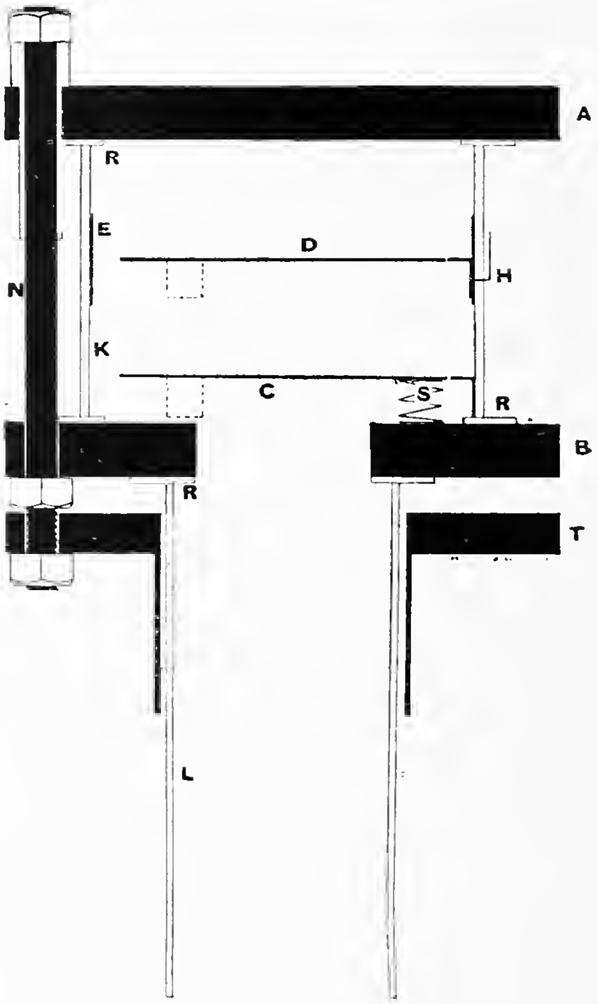

Fig. 3.

indicated in the figure. A thin film of the liquid also spreads over the interior surface of T, and so it is to be expected that the air in T is quickly saturated with its vapour. The beam of light, obtained from an incandescent mantle, I (see also the upper part of fig. 4), with a slit about 1 cm. wide, was focussed inside the test-tube T. All other light was excluded and a black background obtained by means of black velvet. Most of the drops formed by an expansion could be readily seen on looking from E.

Another expansion chamber was used to determine the sign of the charge of the more efficient ionic nucleus. It is drawn to scale in fig. 3. K is a portion of a glass tube, 3·1 cms. in length and 4·2 cms. in diameter, with ground edges. The ends of the chamber are thick aluminium discs, A and B. The joints between these and the glass cylinder K, and between L and B, are made by means of the rubber rings R. Three bolts such as N, insulated from A by vulcanite collars, press the aluminium ends A and B and the connector T against the rubber rings R. The joint obtained in this way is air-tight and remains so. The chamber is divided into an upper and lower half by a thin aluminium diaphragm, D, of 3·6 cms. diameter, supported by three projections pressing against E. Thus there is an annular space 3 mm. wide between the edge of the diaphragm and the wall E. In order to make the lower half of the chamber as similar as possible to the upper, a second diaphragm, C, of the same size as D, is placed over the outlet in the end B, and is connected to B by means of a spiral S of platinum wire. A ring of thin aluminium, E, 1 cm. in width, was placed symmetrically around D, in order to reduce the intensity of the secondary rays from the walls of the vessel, for it is here that the Röntgen rays (mentioned later) are incident. The ends A and B, &c., were made of aluminium with this object, and because the liquids used, when dry and pure, were found not to have any chemical action on aluminium. It it necessary to have the central diaphragm D electrically connected to the exterior of the vessel. A tapered aluminium wire filled a hole in the glass wall at H and was cleated down on the inside and sealing waxed on the outside. The cleated end is in contact with E, which supported D. This gives a joint which protects the sealing wax from the action of the liquids used.

Röntgen rays (see fig. 4) from a large bulb and coil pass through a horizontal slit between two lead blocks 2·8 cms. thick and 0·5 cm. apart. The narrow band of rays thus obtained passes through the ionisation chamber above and below the diaphragm D. The relative positions of the bulb, slit, and expansion chamber were finally adjusted by means of a barium-platino-cyanide screen placed at Y.

With these adjustments made, the shadow at Y of the diaphragm edge-on formed a dark line across the middle of the "image" of the slit.

Separation of Positive and Negative Ions.

The terminals of a two-volt cell were connected to a potentiometer wire (U of fig. 4) of 2000 ohms resistance (with contacts at every 20 ohms), which was connected at the middle to D and to earth. The potential of the top of the expansion chamber and the lower diaphragm C by connecting them to these contacts could be varied between +1 and −1 volt (in steps of 0·02 volt) with respect to the middle diaphragm D. In a number of experiments, the top in one expansion was at −1 volt, and the bottom at +1; in the next expansion the potentials of these plates were reversed.

When the Röntgen rays from the bulb R pass through the slit, they ionise above and below the diaphragm a thin layer of the mixture of air and the vapour present. The secondary rays produced by the primary inside the expansion chamber would produce a few ions throughout all the interior. With the diaphragm earthed, the top negatively and the bottom positively charged, the ions stream as indicated in fig. 4.

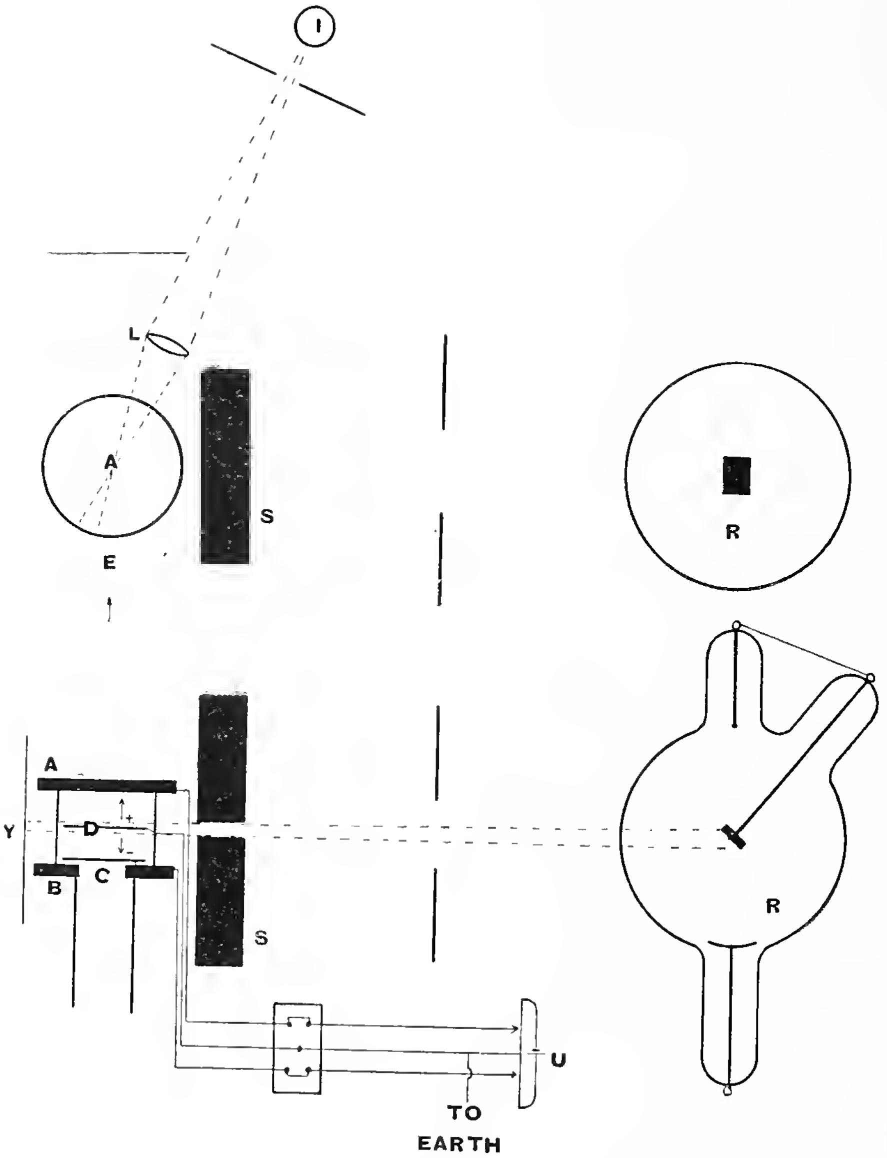

Fig. 4.

If then an expansion be made of the dust-free air and vapour (within one second) after cutting off the Röntgen rays, positive ions will be present in the top partition, and negative in the bottom, which will act as condensation nuclei. It is to be expected that in the top partition the negative ions formed by the secondary rays are removed by recombination with the more numerous positive ions present there.

Observation of the Drops.

The expansion chamber was observed from E (fig. 4) in a direction making a small angle with the beam of light (from the incandescent gas mantle I), which was brought to a focus inside the chamber by means of the lens L. With the eye on a level with the diaphragm D, drops in both the top and bottom partitions of the chamber could be observed at once on a background formed by black velvet.

The switch in the primary of the induction coil, which worked the X-ray bulb at R, was placed close to the handle for "firing" the expansion apparatus, and so with a metronome beating half-seconds the Röntgen rays could be cut off at given intervals before the expansion was made. This metronome was also used for timing the rate of fall of the drops.

Results with Air and Water Vapour.

The following results show that the expansion apparatus is capable of giving results suitable for absolute measurements. (The numbers represent expansions.)

Air Initially Saturated with Water Vapour. Test-tube Expansion Chamber.

No drops: 1·249, 1·253. Drops: 1·256, 1·329, 1·366 (many), 1·376 (fog). Therefore the least expansion for condensation on natural nuclei is 1·256 (1·247), and fog-point 1·376 (1·38).

Röntgen Rays. Expansion Chamber with Aluminium Electrodes.

1·232 no drops, 1·242 four drops seen, 1·246 many drops, 1·246 many. Expansion for Röntgen ray ions 1·246 (1·247).

The values in brackets are those obtained by C. T. R. Wilson. The agreement between the two sets of results is evidence that the expansion in the writer's apparatus is sufficiently rapid to give good results.

Selection of Liquids.

The writer wished to calculate from the results obtained with the liquids he used the supersaturation, and the radius of the nuclei causing condensation, as Mr. Wilson has done for water. To do this it is necessary to know the saturated vapour pressure, π, of the liquid at room temperatures and possibly 50° lower, and also its surface tension and density at this lower temperature. There are not very many liquids for which these have been found. YOUNG and THOMAS[*] have determined a number of constants for ten carefully purified esters. The data required exist or can be calculated for the formic to iso-valeric series of acids. A study of these esters and acids shows how homologous and isomeric compounds behave.

Liquids used.

All the liquids used were KAHLBAUM'S preparations. They were fractionated with a 12-bulbed (pear-shaped) still-head. The boiling-points, at 760 mm. pressure, given differ from those obtained by YOUNG and THOMAS and others partly on account of errors of the writer's thermometers. A more reliable criterion of purity is constancy of boiling-point.

Methyl formate: Dried with phosphorus pentoxide and then fractionated from it. The fraction used boiled from 31°·8 to 31°·9 C. (31°·9 C. YOUNG and THOMAS).

Methyl acetate: Dried with phosphorus pentoxide and fractionated from it. After three fractionations the portion boiling at 56°·9 (57°·15 to 57°·3 YOUNG and THOMAS) was collected and used.

Ethyl acetate: Fractionated from phosphorus pentoxide, the first portion rejected and that boiling at 77°·1 (77°·15 YOUNG and THOMAS) was collected.

Propyl acetate: Dried with phosphorus pentoxide; fractionated twice. The slightly hydrolysed distillate was treated with potassium carbonate, and then with phosphorus pentoxide, and distilled. Boiling-point 101°·4 to 101°·9 (101°·35 YOUNG and THOMAS).

Methyl butyrate: Fractionated; the portion boiling at 102°·9 (102°·8 YOUNG and THOMAS) was distilled from phosphorus pentoxide.

Methyl iso-butyrate: Fractionally distilled, treated with phosphorus pentoxide, and distilled, then with potassium carbonate, followed by phosphorus pentoxide. Boiling-point 92°·4 to 92°·6 (92°·3 YOUNG and THOMAS).

Ethyl propionate: Distilled from phosphorus pentoxide, and redistilled. Boiling-point 98°·9 to 99°·6 (99° YOUNG and THOMAS).

Formic acid: KAHLBAUM'S best acid was used direct from the sealed glass flask it was supplied in. Boiling-point 101°·1 (RICHARDSON 101°·3, SCHMIDT 100°·4, ROSCOE 101°, PERKIN 101°).

Acetic acid: Fractionated five times; final fraction boiled at 118°·5 to 118°·6, but the freezing-point appeared low, indicating the presence of water. The stock acid was then three times crystallised, twice distilled; it then gave a boiling-point of 118° to 118°·05 (118°·5 YOUNG'S "Fractional Distillation"), and a freezing-point of 16°·5 (16°·6 HOLLEMAN'S "Organic Chemistry").

Propionic acid was distilled from phosphorus pentoxide, and twice fractionated. The portion used boiled from 138°·9 to 139°·1 (140°·3 RICHARDSON).

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[*] 'Trans. Chem. Soc.,' 63, 1220 (1893).

n-Butyric acid was fractionated once, and the portion (nearly the whole of the original) boiling between 162°·5 and 162°·6 was used (162°·4 RICHARDSON).

Iso-butyric acid was fractionated. Boiling-point 152°·1 to 152°·6 (153° RICHARDSON).

Iso-valeric was treated with phosphorus pentoxide, and twice distilled. Boiling-point 175° to 176° (175°·3 RICHARDSON, 174°·9 SCHMIDT, 174°·5 LANDOLT).

Amyl alcohol: KAHLBAUM'S (pyridine free) "inactive,"

$$(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}OH,$$

was fractionated. Boiling-point 130°·6 to 131° (131°·4 THORPE, 132° YOUNG and FORTEY, 130°·3 SCHMIDT). Some optically active alcohol was present in the final fraction which gave $[\alpha]_D = -0^\circ{\cdot}5$; for active amyl alcohol $[\alpha]_D = +5^\circ{\cdot}2$.

Least Expansion for Condensation in Air of an Organic Vapour exposed to Röntgen Rays.

The test-tube expansion chamber of glass and mercury, already described (see fig. 2), was used to find the least expansion to produce condensation in a mixture of air and an organic vapour when exposed to Röntgen rays. The air in the carefully cleaned apparatus was dried by placing an open tube containing phosphorus pentoxide inside B (fig. 1). In removing this tube less than 1 mgrm. of water as vapour gained admission to the apparatus. The organic liquid was then admitted by means of the stop-cock funnel (fig. 2) to above the mercury.

The dust present in the apparatus settled out on standing the vessel (say) overnight. It was more quickly removed by small expansions. It is worthy of remark that some vapours could be freed from dust by the latter method distinctly more quickly than others. Thus four or five expansions freed air and ethyl propionate from dust, while air and water vapour have always taken more expansions than that.

Since the writer has found, certainly in the case of some vapours, that the least expansion for condensation depends slightly on the intensity of the Röntgen rays, it is necessary to roughly specify the intensity of the rays used in the experiments to be described. A large bulb with a heavy water-cooled anti-cathode driven by a Marconi induction-coil was used as the source of the Röntgen rays. The alternative spark gap was from 5 to 10 cms. The anti-cathode was 46 cms. from the expansion chamber. The rays had to penetrate the wall—about 0·08 cm. thick—of the glass test-tube expansion chamber.

With some vapours the drops obtained were very minute, so were not readily seen, and did not settle out quickly. With such a vapour it was necessary, after an expansion giving a number of drops, to either wait some time for them to settle out, or to make a small expansion and so condense larger drops on these nuclei left over from the previous larger expansion.

Most of the vapours examined, especially the esters, gave only a few drops with the least expansion producing condensation, and on slightly increasing the expansion the number of drops did not increase as rapidly as they do in the case of water vapour. This makes the least expansion for condensation a less precise point with these vapours than it is with water and substances which behave like it in this respect.

Usually more than one series of experiments were made with each vapour. Examples of the nature of the results obtained are given below, where the different series of observations are combined together.

Air and Ethyl Propionate. Röntgen Rays.

No drops: 1·390, 1·409.

Drops: 1·404, 1·413, 1·426, 1·436, 1·456, 1·477, 1·497.

The apparatus was cleaned and refilled.

No drops: 1·314, 1·400, 1·400, 1·407, 1·408, 1·413, 1·418.

Drops: 1·416 (2 drops seen), 1·420, 1·422.

The first gives the condensation expansion as 1·404, the second as 1·416. Mean **1·410.**

Air and Acetic Acid. Röntgen Rays.

No drops: 1·414, 1·431, 1·439.

With drops: 1·441, 1·446, 1·454, 1·454, 1·497 (fog), 1·507 (fog).

Least expansion for condensation **1·441.**

The drops obtained in these expansions are very small. With feeble Röntgen rays a larger expansion than 1·441 was necessary. These feeble rays were from the same bulb, but the alternative spark gap was 5 cms. instead of 10 cms., and an aluminium screen 2·7 mm. thick was placed between the bulb and the expansion chamber.

Feeble Röntgen Rays.

No drops: 1·446, 1·446, 1·454, 1·471.

With drops: 1·460, 1·471, 1·474, 1·479, 1·482 (many drops).

Least expansion for condensation **1·471.**

This is distinctly larger than the expansion with the more intense rays.

This matter is being further investigated by using γ-rays from radium and from thorium, but the results so far obtained have often been contradictory.

Of the substances tried, acetic acid showed this effect of the intensity of the Röntgen rays on the least expansion for condensation the most.

Summary of Least Expansions for Condensation of Vapours in Air acted upon by Röntgen Rays.

Vapour.	Expansion.	Vapour.	Expansion.
Ethyl acetate	1·486	Formic acid	1·782
Methyl butyrate	1·334	Acetic acid	1·441
Methyl iso-butyrate	1·347	Propionic acid	1·343
Propyl acetate	1·310	*n*-butyric acid	1·380
Ethyl propionate	1·410	Iso-butyric acid	1·360
Iso-amyl alcohol	1·182	Iso-valeric acid	1·220

No very regular relationship can be seen between the constitution of the above vapours and the least expansion necessary to produce condensation in air saturated with them. The expansion, with some exceptions, decreases with increase of molecular weight. On calculating, however, the supersaturation, which exists in the vapour at the moment before condensation takes place, more regular relationships become evident.

Calculation of Supersaturation necessary for Condensation.

The calculation of the supersaturation which exists before condensation takes place has been made for gases saturated with water vapour by Mr. WILSON.[*] When air expands adiabatically, the final temperature is given by the relation

$$\theta_2/\theta_1 = (v_1/v_2)^{\gamma-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where v_1 and v_2 are the initial and final volumes, θ_1 and θ_2 the initial and final temperatures of the air, and γ the ratio of its specific heats; $\gamma = 1{\cdot}404$.

We will assume (the assumption will be discussed later) that this relation gives the final temperature of the mixture of air and vapour in a condensation experiment.[†] This θ_2 then becomes the temperature of the air and vapour at the end of the expansion before any condensation has taken place.

The supersaturation, S, is conveniently defined as the ratio of the pressure of vapour

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[*] 'Phil. Trans.,' A, 189, p. 265, 1897.

[†] *Instantaneous Temperature by a Platinum Thermometer.*—When about half way through this investigation, the writer thought of using a platinum thermometer (after the manner CALLENDAR determines cylinder temperatures) to find the lowest instantaneous temperature produced by an expansion. There appears to be, however, an unsurmountable difficulty. A slight supersaturation would cause condensation on the thermometer wire itself, and the latent heat of condensation would heat the wire. I have seen such condensation actually take place on a hair in the apparatus. A stream of drops fell from it when the expansion was made. The presence of the wire would alter the conditions of the experiment. It certainly would be far more satisfactory to determine the lowest temperatures directly if it were possible.

finally at θ_2 before drops are formed to the pressure of vapour over plane surface of liquid at θ_2, so that

$$S = \pi_1 \frac{\theta_2}{\theta_1} \cdot \frac{v_1}{v_2} \Big/ \pi_2 = \frac{\pi_1}{\pi_2} \cdot \frac{\theta_2}{\theta_1} \cdot \frac{v_1}{v_2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where π_1 is the saturated pressure of the vapour at the temperature θ_1, and π_2 at θ_2. The expansion decreases π_1, to $\pi_1 \, . \, v_1/v_2$, and the temperature falls in the ratio θ_2/θ_1.

In deducing the above formula, and in using it to calculate supersaturations, it is assumed (A) that the final temperature when a mixture of air and vapour expands is given by the relation (I), and (B) that BOYLE'S and CHARLES' laws hold for the vapour. The assumption that BOYLE'S and CHARLES' laws hold for the vapours named on p. 455 seems unavoidable,* since the experimental data do not exist which would enable the supersaturations to be calculated without assuming these laws.

Consider assumption (A): for it to be true, the expansions must be (1) adiabatic, and (2) the formula $\theta_2 = \theta_1 (v_1/v_2)^{1 \cdot 404 - 1}$ must hold for the mixtures of air and organic vapour used.

(1) The expansion is believed to be adiabatic on these grounds: WILSON has most carefully tested the matter, using two very different apparatus, one of which had no piston. The piston of the other was light and the expansion must have been very rapid, certainly more rapid than in the first. The mean of a number of experiments, using air and water vapour gave with each apparatus the same value, 1·252, for the expansion which caught the natural ions present. The writer's result for this point was 1·256, both at the beginning and the end of his experiments. Let θ_2 be the final temperature in these three experiments, if the mean expansion (1·253) were adiabatic, and let the rise of temperature due to the ingress of heat by convection, conduction, and radiation from the walls of the expansion vessel in the different conditions of the three experiments be p, q, r. The actual final temperatures would then be θ_2+p, θ_2+q, θ_2+r, but since in each case these were the temperatures at which condensation just began, they were experimentally the same. Thus p, q, r are too small to be observed, and the expansions were adiabatic. Further, WILSON found $v_1/v_2 = 1 \cdot 38$ for fog-like condensation with air and water, and the writer's apparatus gave 1·376. In these two experiments we have the same final temperature, that necessary for fog-like condensation. The same final temperature is, however, only obtained from equal expansions of 1·38 in different apparatus, when the expansions are not only adiabatic, but are such that the whole lowering of temperature

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* To supply evidence that BOYLE'S and CHARLES' laws are applicable to supersaturated vapours would mean a separate and difficult research. I can think of no direct solution. Professor THOMSON'S determination of $-e$, the charge on a negative ion, is an indirect test of the applicability of these laws in the case considered, for in that method of determining $-e$ the quantity of water condensed by an expansion in ionised air and water vapour is calculated by an application of the gas laws. Dr. H. A. WILSON'S method for $-e$ does not assume those laws. The results of the two methods could be compared. They agree when water vapour is used. Both are subject to large errors.

takes place before any condensation occurs; for otherwise, when the expansion reaches (say, for example) 1·34, drops will be formed on the natural ions present and the temperature will rise with the liberation of the latent heat of condensation, and this rise of temperature will be different in different apparatus. Since actually the final temperatures were the same, we conclude that there was no rise of temperature in this manner and the expansions were strictly adiabatic.

(2) The formula $\theta_2 = \theta_1 (v_1/v_2)^{\gamma-1}$ is for air the expression of the observed results of LUMMER and PRINGSHEIM'S* and MAKOWER'S† experiments, in which θ_2, θ_1, v_1, v_2 were directly observed. With air in an engine cylinder CALLENDAR‡ has observed with a platinum thermometer a change of temperature of as large as 244° C., that is, from $-34°·4$ to 210° C.

A more exact calculation will now be given of θ_2 (for the conditions of experiment given in the next table) when air initially saturated with an organic vapour expands. RICHARZ calculated γ for a mixture of gases. The following indicates how his§ result is obtained. Let the mixture and each component gas have the masses 1, $1-\mu$, μ, the densities (at 760 mm. and a common temperature) ρ, ρ', ρ'', the specific heats at constant volume c, c', c'', the ratio of specific heats, *i.e.*, C/c, γ, γ', γ'', and let R be the gas constant for a gram-molecule (M) of a gas. Then

$$c = c'(1-\mu) + \mu c'' = c' + \mu(c''-c'), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and the specific volume of the mixture is

$$\frac{1}{\rho} = \frac{1}{\rho'}(1-\mu) + \mu\frac{1}{\rho''} = \frac{1}{\rho'} + \mu\left(\frac{1}{\rho''} - \frac{1}{\rho'}\right), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$C - c = \frac{R}{JM} = \frac{1}{\rho}k \quad (k = \text{const.}),$$

since M is proportional to ρ, and R and J are constant. Whence

$$\frac{1}{\gamma-1} = \rho ck', \quad \frac{1}{\gamma'-1} = \rho'c'k', \quad \frac{1}{\gamma''-1} = \rho''c''k' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

By eliminating μ in (3) and (4), and re-arranging terms

$$\rho c(\rho''-\rho') = (\rho-\rho')\rho''c'' + (\rho''-\rho)\rho'c'.$$

Whence by (5)

$$\frac{1}{\gamma-1} = \frac{\rho-\rho'}{\rho''-\rho'}\frac{1}{\gamma''-1} + \frac{\rho''-\rho}{\rho''-\rho'}\cdot\frac{1}{\gamma'-1}.$$

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* SMITH, 'Cont. to Knowledge,' 1903.

† 'Phil. Mag.,' February, 1903, p. 226.

‡ 'Proc. Inst. Civil Eng.,' 131, Pt. I., p. 170 (1897–8).

§ RICHARZ, 'Ann. d. Phys.,' 19, 639 (1906).

This formula has been used to find γ as shown in the following table. In the calculations, as air is one of the component gases,

$$\rho'' = 0{\cdot}00130 \text{ gm./c.c.}, \quad \gamma'' = 1{\cdot}404, \quad \rho' = \tfrac{1}{2} \text{ molecular wgt.} \times 0{\cdot}00009 \text{ gm./c.c.},$$

$$\rho = [\pi_1\rho' + (760-\pi_1)\rho'']/760,$$

where π_1 has the values given in the table on p. 460, have been used.

γ for Air Saturated with a Vapour.

Vapour.	γ'. Observed for vapour.	γ. Calculated by formula.	S.	S_1 if $\gamma = 1{\cdot}404$.
Acetic acid	1·147	1·395	9·3	9·6
Methyl alcohol . . .	1·256	1·382	3·1	3·4
Ethyl alcohol . . .	1·133	1·367	2·3	2·6
Chloroform	1·11	1·264	3	—
Water	1·307	1·401	4·15	4·19

The supersaturation S_1 in the last column is that obtained when $\gamma = 1{\cdot}404$ is used in calculating it. The above values of γ' are from LANDOLT, BÖRNSTEIN, and MEYERHOFFER'S tables, and γ' could not be found for any of the other vapours used in these experiments. Assuming γ' is not less than 1·1* for propionic to iso-valeric acids and propyl to iso-amyl alcohols, it can be shown that S_1 for these substances would have closely the values (S) given in the table on p. 460. For the esters S_1 would be in the same ratio as the values of S given, but would be smaller. For formic $\gamma' = 1{\cdot}27$ has been assumed;† it gives $S_1 = 25{\cdot}1$, while, if $\gamma = 1{\cdot}404$ is used, $S = 26{\cdot}1$.‡

The values for the least expansion for condensation in the case of the alcohols are those of PRZIBRAM (except the value 1·182 for iso-amyl alcohol, which is the writer's), who used both radium and Röntgen rays as ionising agents. Though he does not explicitly state what ionising agent was used to obtain these particular values, it would appear the rays from radium were used in the case of ethyl, propyl, iso-butyl, and iso-amyl alcohols.

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* γ' for iso-butane with 14 atoms in the molecule is 1·108.

† γ' for penta atomic CH_4 is 1·27.

‡ I admit that this application of Richarz' formula is open to criticism. Previously the presence of the vapour has not been taken into account at all. The calculations I give are intended to show that the values for S are not greatly altered when the presence of the vapour is taken into account. The paucity of data (such as the value of γ, and the association constant) for the vapours used in these experiments makes a satisfactory treatment impossible. It is trusted that the calculations given are not without value.

Discussion of Results.

The values of the expansion in the last table are thought by the writer to be accurate to 0·01. An error in a value of the expansion gives rise to a larger error in the value of the supersaturation derived from it. This will be seen on examining the figures for iso-amyl alcohol, for which an expansion of 1·218 means a supersaturation of 5·49, and an expansion of 1·182 an S of 4·02. In this case an error of 0·01 (0·8 per cent.) in the expansion gives rise to an error of 0·4 (8 per cent.) in the supersaturation ; similar figures hold for the other vapours. Besides the error arising from an error in the expansion, another is introduced in the supersaturation in calculating it by the formula

$$S = \frac{\pi_1}{\pi_2} \cdot \frac{v_1}{v_2} \cdot \frac{\theta_2}{\theta_1};$$

for π_2, the saturated pressure of the vapour at the low temperature at the end of the expansion, has to be found in several cases by extrapolation. Though all the vapour-pressure data available have been used, and the inter- and extrapolations have been made with the greatest care by RAMSAY and YOUNG's method, by the Kirchhoff-Rankine formula

$$\log p = A + B/\theta + C \log \theta,$$

and by graphical methods, it has not been possible to obtain very accurate values of π_2[*] in the case of the acids. We cannot expect, then, that the relation between the chemical constitution of a vapour and the supersaturation causing condensation in it to be very precise. Some general relationships, however, seem clear.

Supersaturation and Chemical Constitution.

In the case of the esters and acids the supersaturation decreases with increasing molecular weight. Ethyl propionate, and the isomers butyric and iso-butyric acids, are exceptions to this statement. Of the four isomeric esters, three, namely, methyl butyrate, methyl iso-butyrate, and propyl acetate, have (to quite as high a degree of accuracy as could be expected) the same supersaturation, namely, about 5·2. Ethyl propionate deviates from this value. The isomers *n*-butyric acid and iso-butyric acid have also approximately the same supersaturation.

In the case of the alcohols, after the first of the series the supersaturation increases regularly with the molecular weight, thus :—

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[*] Where π_2 had to be calculated, the extrapolation was made by two of the above-mentioned methods, and in every case these two results were found to agree as closely as the observations of different observers when extrapolated agreed among themselves.

LEAST Supersaturation for Condensation in Air Initially Saturated with Organic Vapours and Exposed to Röntgen Rays.

Vapour.	Formula.	Molecular weight.	Expansion, v_2/v_1.	$\frac{\theta_2}{\theta_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$.	θ_2	Temperature at end of expansion, $t_2°$.	Saturated vapour pressure.		Super-saturation, $= \frac{\pi_1}{\pi_2} \cdot \frac{v_1}{v_2} \cdot \frac{\theta_2}{\theta_1}$.
							π_1 at 17°.	π_2 at $t_2°$.	
Ethyl acetate	$C_4H_8O_2$	88·1	1·486	0·8521	247·1	−25·9	62·6	4·0	8·9
Methyl butyrate . . .	$C_5H_{10}O_2$	102·1	1·334	0·8901	258·1	−14·9	20·6	2·58	5·3
Methyl iso-butyrate . .	,,	102·1	1·347	0·8866	257·1	−15·9	33·0	4·2	5·2
Propyl acetate	,,	102·1	1·310	0·8966	260·0	−13·0	21·2	2·87	5·0
Ethyl propionate . . .	,,	102·1	1·410	0·8704	252·4	−20·6	23·5	1·86	7·8
Formic acid	CH_2O_2	46	1·782	0·795*	230·5	−42·5	26·3	0·479	25·1
Acetic acid	$C_2H_4O_2$	60	1·441	0·8656†	251·0	−22·0	9·8	0·63	9·3
Propionic acid	$C_3H_6O_2$	74	1·343	0·8877	257·4	−15·6	2·00	0·14	9·4
Butyric acid	$C_4H_8O_2$	88·1	1·380	0·8780	254·6	−18·4	0·52	0·022	15·0
Iso-butyric acid . . .	,,	88·1	1·360	0·8832	256·1	−16·9	0·88	0·043	13·3
Iso-valeric acid . . .	$C_5H_{10}O_2$	102·1	1·220	0·9228	267·6	− 5·4	0·20	0·025	6·0
Expansions obtained by PRZIBRAM with Radium and Röntgen Rays.									
Methyl alcohol	CH_4O	32	1·251	0·9181‡	266·2	− 6·8	78·3	18·4	3·1
Ethyl alcohol	C_2H_6O	46	1·175	0·9426§	273·4	0·4	36·9	12·9	2·3
Propyl alcohol	C_3H_8O	60·1	1·178	0·9360	271·4	− 1·6	12·6	3·31	3·0
Iso-butyl alcohol . . .	$C_4H_{10}O$	74·1	1·198	0·9296	269·6	− 3·4	6·8	1·44	3·6
P. Iso-amyl alcohol . .	$C_5H_{12}O$	88·1	1·218	0·9234	267·8	− 5·2	1·78	0·246	5·5
L. ,, ,, . .	,,	88·1	1·182	0·9344	271·0	− 2·0	1·78	0·339	4·1
Chloroform	CCl_3H	119·4	1·54	0·8923‖	258·8	−14·2	143	27·9	3·0

* $\gamma = 1·398$. † $\gamma = 1·395$. ‡ $\gamma = 1·382$. § $\gamma = 1·367$. ‖ $\gamma = 1·264$.

In all other cases $\gamma = 1·404$.

Alcohol.	Supersaturation.	Difference.
Ethyl*	2·56	—
Propyl	3·03	0·47
Iso-butyl	3·66	0·63
Iso-amyl	4·14	0·48

The acids and esters require a larger supersaturation to produce condensation in ionised air than the alcohols do. With the exception of iso-valeric acid, the acids require larger supersaturations than the esters—the supersaturation for formic and the butyric acids being extraordinarily large. One would have expected the association existing in the molecules of the vapour of acetic and some of the other acids to facilitate condensation.

The relations existing between chemical constitution and supersaturation will be seen from the following :—

Esters.	S.	Alcohols.	S.	Acids.	S.
(1) $\mathrm{CH_3{-}\underset{\substack{\| \\ O}}{C}{-}O{-}C_2H_5}$	8·9	(12) $\mathrm{CH_3{-}OH}$	3·12	(6) $\mathrm{H{-}\underset{\substack{\| \\ O}}{C}O{-}H}$	25·1
(2) $\mathrm{C_3H_7{-}\underset{\substack{\| \\ O}}{C}{-}O{-}CH_3}$	5·3	(13) $\mathrm{C_2H_5{-}OH}$	2·56	(7) $\mathrm{CH_3{-}\underset{\substack{\| \\ O}}{C}{-}O{-}H}$	9·3
(3) $\mathrm{(CH_3)_2CH{-}\underset{\substack{\| \\ O}}{C}{-}O{-}CH_3}$	5·2	(14) $\mathrm{C_3H_7{-}OH}$	3·03	(8) $\mathrm{C_2H_5{-}\underset{\substack{\| \\ O}}{C}{-}O{-}H}$	9·4
(4) $\mathrm{CH_3{-}\underset{\substack{\| \\ O}}{C}{-}O{-}C_3H_7}$	5·1	(15) $\mathrm{(CH_3)_2CH{\cdot}CH_2{-}OH}$	3·66	(9) $\mathrm{C_3H_7{-}\underset{\substack{\| \\ O}}{C}O{-}H}$	15·0
(5) $\mathrm{C_2H_5{-}\underset{\substack{\| \\ O}}{C}{-}O{-}C_2H_5}$	7·8	(17) $\mathrm{(CH_3)_2{\cdot}C_3H_5{-}OH}$	4·14	(10) $\mathrm{(CH_3)_2{\cdot}CH{-}\underset{\substack{\| \\ O}}{C}O{-}H}$	13·3
		$\mathrm{H{-}OH}$	4·2	(11) $\mathrm{(CH_3)_2{\cdot}CH{\cdot}CH_2{-}\underset{\substack{\| \\ O}}{C}O{-}H}$	6·0

The general nature of the affect of a given group of elements on the magnitude of S may be stated thus :—

Carbonyl, $>\mathrm{C} = \mathrm{O}$. The presence of this radical is associated with a large S, as shown by the acids and esters.

Alkyl-groups, $\mathrm{CH_3{-}}$, $\mathrm{C_2H_5{-}}$, $\mathrm{C_3H_7{-}}$, $\mathrm{(CH_3)_2CH{-}}$, $\mathrm{(CH_3)_2{\cdot}CHCH_2{-}}$, $\mathrm{C_5H_{11}{-}}$. The presence of these appears to contribute only a small amount to the value of S. The regular increment in S for ethyl, propyl, iso-butyl, and iso-amyl alcohols indicates that

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* Using $\gamma = 1{\cdot}404$ in each calculation.

the effect of these radicals, though small, is proportional to the number of carbon atoms in them. *Hydroxyl*, HO–. This group is present in the alcohols which have the smallest values of S, and in the acids which have the largest values. It may be that when the –OH group is combined with carbonyl carbon in a compound that compound has a large S, while when it is combined with alkyl carbon the value of S is small. S must be known for more varied compounds than the above before this action of hydroxyl can be tested.

Theory of Condensation on Ionic Nuclei.

The theory of the condensation of drops has been given by several writers. Lord KELVIN'S[*] well-known result showed that the surface tension makes the vapour pressure of a small drop greater than that of a large one. Professor J. J. THOMSON,[†] in 1886, deduced an expression for the diminution in the vapour pressure of a drop when it is charged electrically. The combined effect on condensation of the surface tension of a drop and the charge it receives when it condenses on an ionic nucleus has been given by J. J. THOMSON,[†] BLOCH and LANGEVIN,[‡] and C. T. R. WILSON.[§]

Size of Charged Drop in Equilibrium with Saturated Vapour.

Professor THOMSON finds that the vapour pressure of a drop as altered by its charge and surface tension is given by

$$R\theta \log_e \frac{p}{P} = \left(\frac{2T}{a} - \frac{e^2}{8\pi K a^4}\right)\frac{1}{\sigma}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

when T is independent of a, where a is the radius, p the vapour pressure, θ the temperature, e the charge, σ the density, and T the surface tension of the drop; R is the gas constant for unit mass of the vapour, P the pressure of the vapour in equilibrium with a very large drop; K is the specific inductive capacity of the dielectric surrounding the drop.

When the drop is uncharged, *i.e.*, $e = 0$, it will evaporate in the unsupersaturated vapour. When it is charged it increases in size until $p/P = 1$, *i.e.*, $\log_e(p/P) = 0$, or, by (6), until

$$a = \sqrt[3]{\frac{e^2}{16\pi KT}}$$

$$= \sqrt[3]{\frac{3\cdot4 \times 3\cdot4 \times 10^{-20}}{16.\pi.1.76}} \doteq 3\cdot12 \times 10^{-8} \text{ cm.}$$

for water in C.G.S. units, taking $e = 3\cdot4 \times 10^{-10}$ electrostatic units.

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[*] 'Proc. Roy. Soc. Edin.,' 7, p. 63 (1870); also HELMHOLTZ, 'WIED. Ann.,' 27, 508 (1886).

[†] 'Applications of Dynamics to Physics and Chemistry,' London, 1888; 'Conduction of Electricity through Gases.'

[‡] 'Ann. Chem. et Phys.,' [8], IV., p. 135, January, 1905.

[§] 'Smithsonian Report,' p. 195 (1904).

I have calculated a for the following substances :—

RADIUS of Drop with Charge $3 \cdot 25 \times 10^{-10}$ Electrostatic Units in Equilibrium with the Saturated Vapour at 17° C.

	a.		a.
	cm.		cm.
Water	$3 \cdot 02 \times 10^{-8}$	Butyric acid	$4 \cdot 3 \times 10^{-8}$
Ethyl acetate	$4 \cdot 4$	Iso-butyric acid	$4 \cdot 5$
Methyl butyrate	$4 \cdot 4$	Methyl alcohol	$4 \cdot 5$
Methyl iso-butyrate . . .	$4 \cdot 4$	Ethyl alcohol	$4 \cdot 5$
Propyl acetate.	$4 \cdot 4$	Propyl alcohol.	$4 \cdot 5$
Ethyl propionate	$4 \cdot 4$	Iso-butyl alcohol	$4 \cdot 5$
Formic acid	$3 \cdot 8$	Iso-amyl alcohol	$4 \cdot 5$
Acetic acid	$4 \cdot 5$	Chloroform	$4 \cdot 3$
Propionic acid	$4 \cdot 3$		

(Radius of N_2 molecule $1 \cdot 41 \times 10^{-8}$ cm., O_2 $1 \cdot 35 \times 10^{-8}$ cm.)[*]

The surface tensions used in calculating the above tables are from RAMSAY and SHIELDS'[†] and RAMSAY and ASTON'S[‡] determinations, which were made with only the liquid and vapour present in the measuring apparatus.

This value of a is practically the same for the organic liquids, with exception of formic acid. The volume of one of these organic liquid drops would be three times that of the water drop in equilibrium with aqueously saturated air at the room temperature.

Calculated Supersaturation.

According to the theory we are considering, the presence of electrically charged nuclei in a vapour will cause it to condense and form small drops. The charge on these drops tends to make them grow larger, while their surface tension tends to make them evaporate. Their size, when in equilibrium with the vapour, depends on its pressure. There will be a pressure which will enable the drops to grow to such a size that the effect of surface tension will be overcome, and, if the vapour pressure be kept up, the drop will become very large. In a condensation experiment in which the expansion is just sufficient to cause condensation, the vapour pressure at the instant when the expansion ends is sufficient to make the very small (invisible) drops grow to a large size. Professor J. J. THOMSON[§] has shown how this last vapour pressure may be found.

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[*] JEANS, 'Dynamical Theory of Gases,' Cambridge, 1904, p. 340.

[†] 'Phil. Trans.,' A, 184, p. 647 (1893).

[‡] 'Roy. Soc. Proc.,' 56, p. 163 (1894).

[§] 'Conduction of Electricity through Gases,' 2nd Edition, p. 180 (1906).

If c is the radius of a drop (with charge e) which is in equilibrium with the saturated vapour, and a its radius when in equilibrium with the vapour at a pressure p, then

$$R\theta \log_e \frac{p}{P} = 2Tx\,(1-x^3)\,\frac{1}{\sigma c},$$

where $x = c/a$.

For water at 10° C. we have $R = 4{\cdot}62 \times 10^6$, $c = 3{\cdot}05 \times 10^{-8}$ cm., $\sigma = 1$, $T = 74$ dynes/cm., so that for it

$$\log_{10}(p/P) = 1{\cdot}61x\,(1-x^3).$$

The graph of this function (which is typical of the organic vapours as well) is given in fig. 5, where p/P, the supersaturation, is the ordinate, and the abscissa is the radius of the drop with a vapour pressure p. It will be seen that as p/P increases from a very small value to 1, the size of the drop changes very little. When p/P is 5·8, its maximum value, the radius of the drop is 1·6c. Any further increase in p/P makes the drop grow to a very large size, or visible condensation takes place. The AB portion of the curve represents unstable equilibrium, for a increases as p/P diminishes. For condensation to take place, p/P must be slightly greater than its value at A, which is the value of p/P in the above equation when $x\,(1-x^3)$ is a maximum, *i.e.*, when $1-4x^3 = 0$, or $x = 0{\cdot}63$ and $x\,(1-x^3) = 0{\cdot}472$.

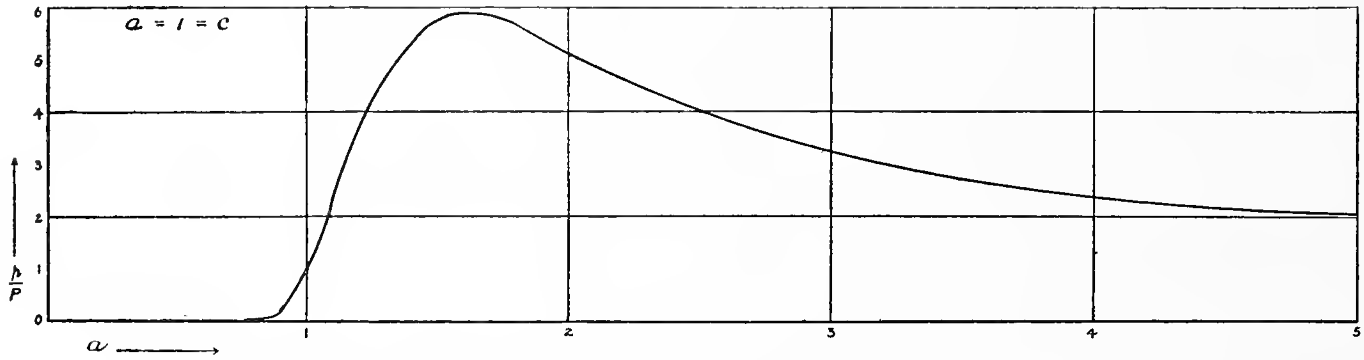

Fig. 5. Radius of charged drop in equilibrium with water vapour at various pressures.

Thus the value of p/P given by the expression

$$\log_{10}(p/P) = \frac{1}{2{\cdot}3}\,\frac{2T}{R\theta c\sigma}\,x\,(1-x^3) = 0{\cdot}41\,\frac{T}{R\theta c\sigma}$$

is the least value which will cause condensation.

The values p/P which the equation gives are stated below for a number of esters, acids, and alcohols. T, the surface tension, was found at the required temperature by plotting RAMSAY and SHIELD'S, and RAMSAY and ASTON'S* values of T at different temperatures; straight lines were nearly always obtained from which the required

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* *Loc. cit.*

SUPERSATURATION Necessary to make a Charged Drop Grow to a Large Size.

Liquid forming drop.	Condensation temperature, $t_2°$.	θ.	R.	σ at t_2, gm./c.c.	T at t_2, dynes/cm.	c at t_2, cm.	S or p/P.	
							Calculated. $\log(p/\mathrm{P}) = 0\cdot41\ \frac{\mathrm{T}}{\mathrm{R}\theta c\sigma}$.	Observed.
Ethyl acetate	−26	247	$9\cdot44 \times 10^5$	0·956	31·8	$4\cdot04 \times 10^{-8}$	28	9
Methyl butyrate . . .	−15	258	$8\cdot15 \times 10^5$	0·935	28·2	4·21	25	5·3
Methyl iso-butyrate . .	−16	257	$8\cdot15 \times 10^5$	0·931	26·8	4·28	21	5·2
Propyl acetate	−13	260	$8\cdot15 \times 10^5$	0·928	27·3	4·25	22	5·1
Ethyl propionate . . .	−21	252	$8\cdot15 \times 10^5$	0·94	28·1	4·21	25	7·8
Formic acid	−43	230	$1\cdot81 \times 10^6$	1·29	43·8	3·63	8	26
Acetic acid	−22	251	$6\cdot93 \times 10^5$	1·09	25·9	4·32	13·5	9·3
Propionic acid	−16	257	$1\cdot12 \times 10^6$	1·03	29·6	4·14	10	9·3
Butyric acid	−18	255	$9\cdot44 \times 10^5$	0·997	29·4	4·15	16	15
Iso-butyric acid . . .	−17	256	$9\cdot44 \times 10^5$	0·987	27·5	4·24	13	13
Methyl alcohol	− 7	266	$2\cdot6 \times 10^6$	0·826	25·4	4·36	2·6	3·1
Ethyl alcohol	0	273	$1\cdot81 \times 10^6$	0·81	23·8	4·45	3·5	2·3
Propyl alcohol	− 2	271	$1\cdot38 \times 10^6$	0·821	25·3	4·36	6	3·1
Iso-butyl alcohol . . .	− 3	270	$1\cdot12 \times 10^6$	0·823	24·4	4·42	8	3·7
Iso-amyl alcohol . . .	− 5	268	$9\cdot4 \times 10^5$	0·835	25·2	4·37	13	5·5
Chloroform	−14	259	$6\cdot97 \times 10^5$	1·58	31·8	4·04	16	3·0
Water	− 8	265	$4\cdot62 \times 10^6$	0·999	76·7	3·01	7·1	4·2

value of T could be found. The densities given[*] were corrected for temperature by using the observed coefficients of expansion. In this equation R for oxygen would be $2{\cdot}6 \times 10^6$, and for a gas of molecular weight M is $2{\cdot}6 \times 10^6 \times 32/M$. The molecular weight of acetic acid has been taken as 120, as found by BINEAU and RAMSAY and YOUNG.[†] The values of c, the radius of a drop with charge e in equilibrium with its saturated vapour, in the preceding table are slightly different to those given previously, for c varies a little with the temperature, which in this table is t_2, the temperature at which drops are formed in the expansion experiments.

Discussion of Calculated and Observed Supersaturations.

In calculating the supersaturation in the last table no account has been taken of the variation of surface tension with the thickness of the surface film. REINOLD and RUCKER'S observations show that the surface tension T of a water film begins to depend on the thickness when the film is about 10^{-5} cm. thick. For thicknesses less than this T diminishes, but passes through maxima when the film is $1{\cdot}2 \times 10^{-6}$ and when 6×10^{-7} cm. (Johannot) thick. Lord RAYLEIGH,[‡] however, found that one interpretation of his experiments led to the conclusion that an oil film only one molecule thick still had surface tension. The equation $\log (p/P) = 0{\cdot}41T/R\theta\sigma c$ has been applied above to drops of about 7×10^{-8} cm. radius. It is to be expected that T for the surface films of such drops has a smaller value than for thick films. This would lead to a calculated value of p/P, that is of S, which would be too large—a difference that the last table exhibits, for in all but two cases (formic acid and methyl alcohol) the calculated value of S is larger than the observed. On this view we would conclude that the surface tensions of acetic, propionic, butyric, and iso-butyric acids do not vary with the thickness of the surface film, since the calculated value of S for these acids agrees with the observed.

Condensation on Natural Nuclei.

The least expansion producing condensation in the absence of Röntgen rays was determined with the mercury sealed test-tube expansion chamber of fig. 2. The following is an example taken at random of the observations obtained.

Dust-Free Air Saturated with Ethyl Acetate. Natural Nuclei.

Expansions v_2/v_1.

Without drops: 1·390, 1·506, 1·511, 1·524, 1·526, 1·531.
With drops: 1·528, 1·534, 1·536, 1·542, 1·545, 1·556, 1·587.
Least expansion for condensation 1·528.

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[*] VAN NOSTRAND'S 'Chem. Ann.'

[†] 'Trans. Chem. Soc.,' 49, p. 790 (1886)

[‡] 'Phil. Mag.,' October, 1899, p. 23

The results of these experiments, as a whole, were more regular than those obtained when the air and vapour were ionised by Röntgen rays. The number of expansions made in order to determine v_2/v_1 varied from 7 to 20 for the different substances, and on the average was 14.

After acetic acid had been exposed to the rays from radium or from thorium very inconsistent observations were obtained.

The vapour pressure π_1 of tertiary amyl alcohol was assumed to be between 5 and 15 mm. at 17° C.* in order to calculate the expansion.

Air and Water. Natural Nuclei.

No drops: 1·242, 1·242, 1·250, 1·252, 1·254.

Drops: 1·256, 1·258, 1·260, 1·262, 1·262, 1·266.

Least expansion for condensation **1·256.**

C. T. R. Wilson,† using a small apparatus, found 1·252. Immediately before the above experiments the following observations were obtained with the apparatus, the air and water vapour being exposed to Röntgen rays during the expansion.

Air and Water. Röntgen Rays.

No drops: 1·208, 1·218, 1·220, 1·224, 1·226, 1·230, 1·230, 1·234.

Drops: 1·236, 1·240, 1·240, 1·241, 1·252 (thin cloud).

Thus least expansion for condensation is 1·236; 1·247 (Wilson).‡ The least expansions for condensation found from experiments just described are given in the second column of the table on the following page.

The nuclei in the condensation we are considering must be the natural ones present in the dust-free air. Wilson found, as we saw earlier in this paper, the same expansion caught the natural nuclei as caught the nuclei produced by Röntgen, Becquerel, and other rays; and he showed also that the natural nuclei could be removed by an electric field, so they were the ions which normally exist in the air.

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* The vapour pressure of tertiary amyl alcohol at 17° C. has not been determined. It may be calculated thus: If ${}_{A}\theta_{\pi}$ represents the absolute temperature when a liquid A has a vapour pressure π, then we know that

$$ {}_{\text{water}}\theta_{760}/{}_{\text{tertiary amyl alcohol}}\theta_{760} = 373/374\cdot 8 = 0\cdot 9975. $$

Now this ratio is known to vary only slightly with the temperature; for several alcohols it changes $+0\cdot 0002$ per degree. Therefore the temperature of water when it has the same vapour pressure as tertiary amyl alcohol at 17° is

$$ {}_{\text{water}}\theta_{\pi} = {}_{\text{tertiary amyl alcohol}}\theta_{\pi} \times 0\cdot 98 = 290 \times 0\cdot 98 = 284^{\circ}. $$

But at $273^{\circ} + 11^{\circ}$ π for water is 9·8 mm. So, according to this reasoning, π for tertiary amyl alcohol at $273 + 17$ is 9·8 mm.

† 'Phil. Trans.,' A, 189, p. 265 (1897).

‡ 'Phil. Trans.,' A, 192, p. 408 (1899).

With the substances used by the writer in every case a larger expansion (as is shown in the following table) was necessary to cause condensation in air not acted on by Röntgen rays than in air so acted on.

LEAST Expansion for Condensation.

Vapour.	Without rays.	With Röntgen rays.	Difference.
Ethyl acetate	1·528	1·480	0·048
Methyl butyrate	1·364	1·334	0·030
Methyl iso-butyrate	1·387	1·347	0·040
Propyl acetate	1·334	1·310	0·024
Ethyl propionate	1·438	1·410	0·028
Formic acid	1·865	1·782	0·083
Acctic acid	1·508	1·441	0·067
Propionic acid	1·369	1·343	0·026
n-Butyric acid	1·463	1·380	0·083
Iso-butyric acid	1·403	1·360	0·043
Iso-valeric acid	1·256	1·220	0·036
Iso-amyl alcohol	1·210	1·182	0·028
Water	1·256	1·236	0·020

Natural and Röntgen-Ray Nuclei.

The differences between the expansions necessary to catch natural and Röntgen-ray nuclei arises partly probably from the size of the expansion chamber. We have seen (p. 445) that, by using a large apparatus, WILSON found for air and water vapour that the expansion for the natural nuclei was the same (1·247) as for Röntgen-ray ionic nuclei. Thus the differences in the table above must arise partly from the size of the apparatus. In the experiments made by the writer to determine the natural nuclei point in aqueously saturated air only a few drops were seen with the smaller expansions (1·256 one drop, 1·258 five or six drops, 1·260 one). Further, it was found that a drop may be formed and not be seen if the observer's eye has been exposed to anything but feeble light immediately before or during the experiment. Thus the small number* of natural nuclei (and consequently of drops) which are dealt with in these experiments lead to a value for the expansion required to catch the natural nuclei which is too large. This difficulty does not arise with the far more numerous Röntgen-ray nuclei. While it is thought that the above factors may account for the differences of 0·02 in the last table, they can scarcely account for the larger differences for formic (0·08), acetic (0·07), and butyric acids (0·08). These differences are very probably

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* The natural ionisation in hydrogen in a closed vessel is only 0·18 of that of air [WILSON, 'Proc. Roy. Soc.,' 69, p. 277 (1901)], and consequently WILSON did not observe condensation on the natural nuclei in it.

connected with the phenomena that the least expansion necessary to catch the nuclei produced in air and acetic acid vapour depends on the intensity of the Röntgen rays. Thus the least expansion for condensation in this acid with intense X-rays was found to be (see p. 454) 1·441, and with feeble rays 1·471. Now the radiation which produces the natural ionisation in air is largely due to a penetrating radiation[*] of very small intensity. It will be necessary to make a special investigation to clear up the question of the relative efficiency of the natural nuclei and the Röntgen-ray ionic nuclei in case of formic, acetic, and butyric acids.

Professor BARUS[†] observed, in 1906, that the intensity of the Röntgen rays similarly affects condensation in air and water vapour.

In the table on p. 470 the least supersaturations which will produce condensation on the natural nuclei have been calculated. $\gamma = 1·404$ has been used in each case.

The values of π_2 used in this paper have been inter- and extra-polated by the method of RAMSAY and YOUNG, the Kirchhoff-Rankine formula, and graphically. π_2 of each substance is for a lower temperature in the table on p. 470 than in the case of the table on p. 460, and consequently the above values of the supersaturation are less accurate than those given in the latter table. For this reason the relation of S to chemical constitution is discussed for condensation in air ionised by Röntgen rays. It will be seen, however, that the supersaturation necessary for condensation on natural nuclei is related in essentially the same way to the chemical constitution of the vapour as in the case already discussed.

Sign of the Charge of the more Efficient Nucleus.

It has been mentioned how C. T. R. WILSON found that a smaller supersaturation gave condensation on the negative ion than on the positive in air initially saturated with water, or, in other words, how he found the negative ion to be the more efficient nucleus for water vapour.

The chief difficulty encountered in finding the more efficient ion for organic vapours was to make an expansion chamber of material which is unacted upon by them. Sodium silicate, lead oxide and glycerine, sealing wax, rubber dissolved in benzine, were tried as cements for the joint between the aluminium and glass in the apparatus described on p. 449; the two first, which were not acted upon by esters, failed to make a permanently gas-tight joint. Sealing wax and rubber are acted upon by many organic liquids. If, however, the vapour only of the ester (say) is allowed to come in contact with the rubber, the action is very slow and the rubber appears unaffected. A sensitive method of detecting the action of the ester on the rubber is to determine the expansion necessary to catch X-ray nuclei immediately after filling the apparatus with the ester, and then again twenty-four hours or so later; a change

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[*] MCLENNAN, 'Phys. Rev.,' 16, p. 184 (1903); RUTHERFORD and COOKE, *ibid.*, 16, p. 183 (1903).

[†] 'Physical Rev.,' 22, 2, February, 1906.

Least Supersaturation for Condensation on Natural Nuclei in Dust-free Air Initially Saturated with Organic Vapours.

Vapour.	Formula.	Molecular weight.	Expansion, v_2/v_1.	$\frac{\theta_2}{\theta_1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$, $\gamma = 1\cdot404$.	θ_2.	t_2.	π_1 at 17°.	π_2 at t_2.	Super-saturation, $S = \frac{\pi_1}{\pi_2} \cdot \frac{v_1}{v_2} \cdot \frac{\theta_2}{\theta_1}$.
Ethyl acetate	$C_4H_8O_2$	88·1	1·528	0·8426	244·4	−28·6	62·6	3·31	10
Methyl butyrate . . .	$C_5H_{10}O_2$	102·1	1·364	0·8821	255·8	−17·2	20·6	2·19	6
Methyl iso-butyrate . .	,,	102·1	1·387	0·8762	254·1	−18·9	33·0	3·44	6
Propyl acetate . . .	,,	102·1	1·334	0·8900	258·1	−14·9	21·2	2·47	5·7
Ethyl propionate . .	,,	102·1	1·438	0·8635	250·4	−22·6	23·5	1·65	8·6
Formic acid	CH_2O_2	46	1·865	0·7774	225·4	−47·6	26·3	0·302	37
Acetic acid	$C_2H_4O_2$	60	1·508	0·8471	245·7	−27·3	9·8	0·407	13·5
Propionic acid . . .	$C_3H_6O_2$	74	1·369	0·8808	255·4	−17·6	2·00	0·128	10
Butyric acid	$C_4H_8O_2$	88·1	1·463	0·8575	248·7	−24·3	0·52	0·0125	25
Iso-butyric acid . . .	,,	88·1	1·403	0·8721	252·9	−20·1	0·88	0·029	19
Iso-valeric acid . . .	$C_5H_{10}O_2$	102·1	1·256	0·9120	264·5	− 8·5	0·20	0·016	9

in the value of the expansion is an indication that the ester has acted on the rubber. Acetic acid and inactive amyl alcohol (iso-butyl carbinol), when tested in this way, and when tested directly, were not found to act on the rubber used in the writer's apparatus.

All the vapours tried condensed more readily in air on the positively charged nuclei than on the negative, as is seen below. Röntgen rays were the ionising agent.

Vapours which Condense with a Smaller Supersaturation on the Positive Nucleus than on the Negative.

Ethyl acetate, methyl butyrate, propyl acetate, acetic acid, amyl alcohol ("inactive").

Przibram (*loc. cit.*) has found in addition to the above :—

Methyl alcohol, ethyl alcohol, iso-amyl alcohol, heptyl alcohol, chloroform, ethyl iodide.

It is remarkable that there is only one vapour (water) so far known which condenses more readily on the negative than on the positive ion.

Bubbling Experiments.

Lenard* showed that when water splashes against a metal plate it charges the plate positively and the surrounding air negatively; a little later Lord Kelvin† observed the electrification produced by air in bubbling through water—the air became negatively and the water positively charged. The air near the Niagara Falls is known to be strongly negatively charged. Professor Thomson‡ has suggested a double-layer theory to account for these observations. "When air bubbles through water, or when the area of a drop is suddenly increased by the splashing of the drop against a plate, a virgin surface of the water is exposed to the air; if, as seems to be the case, a double layer of electricity is formed at this surface, and if the ions in the layer next the air come from the air, then there must be left in the air an excess of negative ions if the outer coating is positive, and of positive if the outer coating is negative." On this view for a water drop the negative layer is next to the water and the positive layer to the air.

Professor Thomson§ has further pointed out that if this double layer exists at the surface of an ionic condensation nucleus, and if the layers are in the same order on both positive and negative nuclei, then the relative efficiency of the nuclei will not be the same. For example, if the water nuclei have the negative layer inside, as indicated by the bubbling and dropping experiments, then the negative ion will be a

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* 'Wied. Ann.,' 46, p. 584 (1892).

† 'Roy. Soc. Proc.,' 57, p. 335 (1895).

‡ 'Conduction of Electricity through Gases,' 2nd Edition, p. 428.

§ *Loc. cit.*, p. 186.

more efficient nucleus for the condensation of water vapour than the positive, for in this case the field of the negative nucleus due to the ionic charge is in the same direction as that due to the double layer; while for the positive nucleus these fields are in opposite directions. In the first case the effect of the charge in making the ion efficient as a condensation nucleus is increased, and in the second it is diminished. Thus the double-layer theory requires, in order to account for the observed greater efficiency of the negative nucleus than the positive, that the negative layer on a water drop should be next to the water and the positive layer next to the air. This we have seen is also the arrangement of the layers to be expected from the fact that water becomes positively charged when bubbled. In other words, this theory requires that the sign of the charge acquired by air, when it is bubbled through a liquid, should be the same as the sign of the charge on the more efficient nucleus for the condensation of the vapour of that liquid.

The eleven liquids mentioned on p. 471 have been found by PRZIBRAM and myself to condense on the positive nucleus more readily than on the negative. In the case of these substances the theory requires that when air is bubbled through them the liquid should become negatively charged. When the liquids were bubbled, all that were tried, with exception of acetic acid, became negatively charged in agreement with the theory.

Ethyl alcohol is the only one of the liquids which had been previously examined in this way; LENARD found in two experiments with alcohol containing 9 per cent. of water the electrification on bubbling to be once $-0{\cdot}039$ and once $+0{\cdot}123$ in terms of his unit.

In the writer's experiments a small wide-mouthed bottle was insulated by attaching it with sealing wax to a disc of vulcanite. A foot bellows, which gave a sufficiently uniform pressure, forced air through two tubes containing cotton wool, calcium chloride, and solid caustic soda. The dust-free and dry air passed through a vulcanite tube insulator to a glass tube which dipped below the surface of the liquid in the bottle. When the bellows were in action, a steady stream of bubbles was formed in the liquid. The electrification produced was detected by attaching a wire dipping in the liquid to one pair of quadrants of a Dolezalek electrometer which gave from 4000 to 5000 mms. deflection per volt on a scale at about 2 meters. The bottle and wire were shielded from inductive effects by an earthed metal vessel. The drift of the spot was generally observed for four minutes while the air was bubbling through the liquid and for the same time without bubbling. The difference in the drift gave the electrification due to the bubbling. For nearly all the liquids tried the effect was larger the first time the liquid was bubbled than for subsequent bubblings. For methyl and ethyl alcohols the electrification was small and could just be detected with certainty.

It was found that different samples of KAHLBAUM'S I methyl alcohol, which had been distilled after drying over lime, became sometimes positively and sometimes negatively electrified. But when some of this alcohol was carefully purified—(1) by conversion into methyl oxalate and by subsequent hydrolysis, (2) by distillation after treatment with sodium—both products behaved alike and became negatively charged. The sign of the charge acquired by the liquids which have been examined when bubbled was as follows :—

ELECTRIFICATION on Bubbling.

Liquid.	Sign of charge acquired by liquid.	Liquid.	Sign of charge acquired by liquid.
Methyl alcohol	–	Methyl butyrate	–
Ethyl alcohol	–	Acetic acid	+
Iso-amyl alcohol	–	Chloroform	–
Ethyl acetate	–	Ethyl iodide	–
Propyl acetate	–		

Purification of Liquids.

Methyl alcohol : (1) KAHLBAUM's alcohol was converted into methyl oxalate by anhydrous oxalic acid; the resulting oxalate was washed and hydrolised by sodium hydrate. The alcohol obtained was distilled, and then distilled from lime. (2) The same initial alcohol was treated with metallic sodium, and distilled.

Ethyl alcohol : Distilled from lime from marble, and then from a small piece of sodium. Density at 12°, 0·7961 gms. per cubic centimetre. (Absolute alcohol has a density of 0·7962.)

Chloroform : Twice distilled, boiling point 61·7° to 61·8° at 777 mm.

Ethyl iodide : Once distilled.

The other liquids were the same as were used in the condensation experiments (see p. 452).

The result for acetic acid is not in agreement with the double-layer theory, though the acid used had been purified by fractional crystallisation and distillation. It has been mentioned that other anomalous results have been obtained with this acid.

Fog-like Condensation.

Some observations were made to find the expansion necessary for fog-like condensation in certain organic vapours. But the point at which this kind of condensation took place was not usually sufficiently well defined for the results to be very exact; for, as the expansion was increased above that which caught the natural nuclei, the number of drops continuously increased. In this respect acetic, propionic, *n*-butyric, and iso-valeric acids, methyl butyrate, and propyl acetate are unlike water. Tertiary amyl alcohol behaves more like water: with it an expansion of 1·27 gives many drops, the condensation becoming fog-like when the expansion is increased 1·28.

Summary.

(1) The least expansion which causes condensation in air initially saturated with an organic vapour and ionised by Röntgen rays has been determined for five esters, six acids (formic to iso-valeric), and iso-amyl alcohol.

(2) In the case of acetic acid the expansion required was greater for feeble X-rays than for more intense ones.

(3) The supersaturation S existing at the end of each of the expansions mentioned in (1) has been calculated, and also for four alcohols and chloroform, from PRZIBRAM's experiments.

(4) The acids are found, on the whole, to have the largest values of S and the alcohols the least. The isomers examined have the same value for S, with one exception. In the case of the alcohols, ethyl to iso-amyl, a fairly regular decrease in S accompanies the addition of a CH_2 group.

(5) The existing theory of condensation on ionic nuclei has been given, values of S have been calculated from it, and compared with S deduced from the observed expansions. The agreement in the case of acetic, propionic, *n*-butyric, and iso-butyric acids and methyl alcohol is very close.

(6) The expansion and supersaturation necessary for condensation on the natural nuclei have been determined for the same (dust-free) vapours. In the case of formic, acetic, and butyric acids a distinctly greater expansion is required to catch the natural nuclei than that required for the ionic nuclei produced by Röntgen rays.

(7) As the expansion was increased in the absence of artificial ionisation the number of drops usually increased continuously with it, so that the fog-point was ill defined, except in the case of tertiary amyl alcohol.

(8) Ethyl acetate, methyl butyrate, propyl acetate, acetic acid, iso-amyl alcohol were found to condense for a smaller supersaturation on the positive nucleus than on the negative. Water is the only known substance for which the negative ionic nucleus is more efficient than the positive.

(9) On bubbling air through methyl, ethyl, and iso-amyl alcohols, ethyl acetate, propyl acetate, methyl butyrate, chloroform, and ethyl iodide they became negatively electrified. This was the sign of the electrification to be expected from Professor THOMSON's double-layer theory of the relative efficiency of ionic nuclei.

I wish to thank Mr. C. T. R. WILSON for most helpful discussion, and Professor THOMSON for many suggestions and his inspiring interest.

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Principal Contents:—List of Fellows, Committees, &c.; Statutes and Regulations; Business of the Society during 1907, including Anniversary Meeting, Council's Report, and Treasurer's Accounts; Arrangements for 1908.

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XIII. *The Absorption Spectra of the Vapours of Benzene and its Homologues, at Different Temperatures and Pressures, and of Solutions of Benzene.*

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[PLATES 32–33.]

INTRODUCTION.

THE absorption spectrum of benzene in a state of vapour and in solution was photographed by W. A. MILLER ('Phil. Trans.,' 1862, vol. 152, II., pp. 861–887). It was also photographed by me in 1880 ('J. Chem. Soc.,' 1881, vol. 39, p. 153; 1882, vol. 41; 1885, vol. 47, pp. 685–757), with the instrument and by the method described in the 'Scientific Proceedings of the Royal Dublin Society' in 1881 (vol. iii., p. 93, New Series) and 'J. Society of Arts,' 1885. For these investigations a molecular weight in milligrammes was employed to test the molecular absorption of the hydrocarbon, but the quantity of vapour was too large even at low temperatures, and the temperature, as since ascertained, was in other experiments too high to admit of the numerous absorption bands being observed, although a series of bands had been photographed from very dilute solutions of benzene in alcohol. The continuous rays which accompany the lines in the emission spectrum of the strongly condensed spark of cadmium were found to afford the best source of light in the region of short wave-lengths.

J. PAUER, in 1897 ('WIEDEMANN'S Annalen,' vol. 61, p. 363), also used the cadmium spectrum precisely in the same manner for a more complete investigation of benzene and its homologues, but his experiments were not quantitative, although he compared the same substances in the states of vapour, of liquid, and in solution at a temperature of 20° C. He accurately measured 29 different narrow bands characteristic of the spectrum of the vapour of benzene. More recently this work has been repeated by WILHELM FRIEDERICHS ('Zeitschrift f. Wissenschaftl. Photographie,' 1905, vol. 3, p. 154) and by LEONARD GREBE (*loc. cit.*, 1905, p. 363).

FRIEDERICHS used a quartz vacuum-tube containing hydrogen as a source of continuous rays; while GREBE used the continuous spectrum described by KONEN, when a powerful spark is passed between poles of aluminium immersed in water. The exposure necessary in FRIEDERICHS' experiments was from 12 to 21 hours, in GREBE'S from $\frac{3}{4}$ to 1 hour. Only the maximum of absorption of the bands was measured by these investigators and not their width, but the widening of the bands is an important feature in the spectrum when changes of temperature and pressure occur. I have re-investigated the vapours of the aromatic hydrocarbons recently by means of the continuous rays emitted by condensed sparks passed between various electrodes, but for measurements in the ultra-violet the cadmium continuous spectrum which accompanies the lines of that element has alone been employed, because it has been found, on the whole, to yield the most satisfactory results.*

The vapours of benzene and some of its derivatives have been examined (1) at different temperatures and constant pressure, and (2) at different pressures, the temperature being constant. The several different spectra photographed prove the correctness of the previous measurements of PAUER, FRIEDERICHS, and GREBE, though these do not show complete agreement among themselves.

Thus the band at wave-length 2694 (FRIEDERICHS) is a real one and not, as GREBE believed, a mere marking or scratch on the photographic film; also the band at 2631 observed by FRIEDERICHS is undoubtedly a benzene band; so likewise are those at 2633 and 2638 observed by GREBE, but believed by him to be due to an impurity.

Experimental.

The benzene was a portion of 2 litres obtained from Kahlbaum which had been crystallised and was free from thiophene. A quantity of 250 c.c. was recrystallised, the crystals being pressed between folds of blotting paper, melted and redistilled. Its boiling-point was constant at 81° C. and 763 mm. barometric pressure.

The Absorption Spectra at Varying Temperatures.

An arrangement was used similar to that employed by PAUER, with the exceptions that the tube was of bronze 150 mm. long, fitted into a rectangular water-bath which was deep enough to hold the small flask of benzene as well as the immersed tube; also the metal tube was closed at each end by a quartz plate cemented on to a flange with seccotine, or fish glue, and could be exhausted, partially or completely, at any temperature.

The bath in different experiments, according to the temperature required, was filled with water or glycerine. Brazed to the bronze tube were two smaller tubes for inlet and outlet of air or a neutral gas. The inlet was connected with the side tube of the flask containing the benzene, the outlet with a reversible aspirator which holds

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* 'Roy. Soc. Proc.,' 1906, A, vol. 78, pp. 243–245. PAUER arrived at the same conclusion, see footnote on p. 365 *loc. cit.*

1 litre of water. The volume of air aspirated through the benzene in each experiment could be exactly measured; it served to vaporise the liquid and charge the tube with vapour. After using the aspirator for a few minutes the taps were closed and the temperature taken by a thermometer kept in the bath, the liquid in which was constantly stirred. In front of the end of the tube is a quartz lens, and behind the lens the electrodes which give the emission spectrum, the rays being focussed upon the slit of a quartz spectrograph.

The plates were exposed from two to five minutes, but as a rule the exposure was not more than two minutes. After one exposure the temperature of the bath was raised and another exposure made immediately below the first, and so on, going through the same manipulations as for the previous exposure. From the vapour-pressure curve and the ascertained temperatures in the bath the quantity of benzene presumably in the tube at each exposure was calculated.

The actual quantity of the hydrocarbon present in the tube was afterwards determined by the gas analysis of its contents at the different temperatures.

The capacity of the tube was 79 c.c. and its length 150 mm. It will be seen that, as the calculated and found quantities at 12°·7 C. are very nearly the same, the molecule of benzene in a state of vapour is the same at temperatures below its boiling-point as at 20° C. above it. At higher temperatures the analytical data show that the air was far from saturated with the vapour, inasmuch as at 53° C. there were only 6 mgrm. more of benzene in 79 c.c. than at 12°·7 C., whereas the calculated quantity is 72 mgrm. more.

THE Contents of the Tube.

Temperatures.	Vapour pressures of benzene.	Weight of benzene.	
		Calculated.	Found.
° C.	mm.	grm.	grm.
12·7	53	0·0184	0·0179
25·7	95	0·0316	0·0203
43	205	0·0643	0·0211
53	297	0·0904	0·0239

As the results of the gas analyses were not altogether of a character to be relied upon, another series of determinations was made by burning the vapour in a combustion tube with cupric oxide and weighing the products of combustion. In this way also it was found that the results obtained were very irregular, and after many combustions had been repeated, which yielded figures varying in an unaccountable manner, it was concluded that to ensure a determination of the amount of benzene under examination in each case a very complicated apparatus would have to be constructed, all the tube connections being of metal or of glass. It must not be overlooked that the time occupied in making the analyses was much longer than in taking the photographs, and as the vapour had to be transferred from one vessel to another, this admitted of changes occurring in the composition of the vapour, by condensation at one period and saturation at another. Moreover, at low pressures there was a difficulty experienced in extracting all the vapour from the tube and submitting it to analysis.

The Absorption Spectrum of Benzene Vapour at Constant Temperature and Reduced Pressures.

In the first experiments at reduced pressures a glass tube was used with glass taps, the same arrangement being used for vaporising the benzene, but the outlet tube, instead of being connected with an aspirator, was connected by a glass T-piece with a filter-pump and a pressure gauge. Air was drawn through the benzene and regulated by the flow from the pump until the mercury in the gauge was steady; the exhaustion still proceeding, the exposure of the plate was made, after which the exhaustion was continued until a steady and further reduction in the pressure was obtained, when another exposure was made, and so on. In this way the vapour was continually being removed at one end of the tube and renewed at the other, but always at the same pressure for each exposure. Photographs were taken at temperature 11°·5 C., and 778 mm., 483 mm., 253 mm. and 21 mm. pressure. It was observed that in the first series of experiments the photographs taken at reduced pressures were all somewhat weak, and the tube for working at low pressures would probably be improved by being lengthened to render the absorption bands more distinct. The spectra were photographed on Cadett and Neale's spectrum plates, developed with ferrous oxalate, and cleared with a solution of alum acidified with nitric acid. Some few photographs were taken on "Rainbow" Warwick plates, the period of exposure being the same in each case, namely, two minutes.

The Measurement of the Spectra.

The plates were measured with a micrometer made many years ago by the late Mr. A. HILGER, the screw of which, according to my instructions, was made of platinoid, because this metal is rustless. The pitch of the screw is 100 turns to the inch. It carries a microscope made by Zeiss, which has fine definition and a flat field. The instrument is fitted on a stand tilted at an angle of 45° C. to facilitate prolonged observation through the microscope. Measurements to the 1/10,000th of an inch are easily made; but in the case of absorption bands this cannot always be accomplished, because it is difficult to determine, under the necessary magnification, where the bands begin and end. The wave-length at the edges on each side of a band were measured whenever they were broad enough and well-defined. In some cases two very narrow bands were seen so close together that the space between them could not be measured, and this explains why they have been assigned the same wave-length. In like manner, where a rather broad band ended and another commenced, it was found impossible to measure the two points with certainty, although an extremely narrow space could be seen between them. Each spectrum was measured twice independently, and the bands for the most part were described. For constructing an interpolation curve, the spectra of lead, tin, and cadmium were photographed with a very narrow slit and short exposure with a self-induction coil in circuit, by which means the spark lines were rendered sharp and narrow. But as the locus of the foci lies exactly in the same plane, the 18 lines of cadmium between Cd 17 and Cd 26 are alone sufficient, and latterly were adopted.

The linear dispersion on the original spectra is such that between Cd 17, λ 2748·68, and Cd 26, λ 2144·44, there are 2781·1 linear divisions of the micrometer scale = 2·7011 inches, which are equivalent to a difference of 604·24 Ångström Units between the above wave-lengths. The dispersion at the less refrangible end, Cd 17, increases from 3·3 divisions to 6·3 divisions for 1 Ångström Unit at the more refrangible end, Cd 26.

When the wave-length measurements had been tabulated in the usual manner, it appeared as if the bands in the different spectra of the same substance bore no relation to each other; accordingly, they were rearranged in four columns, so that obviously related bands or groups fell upon the same horizontal lines or thereabouts, and the changes in the spectra caused by increase of temperature or diminution of pressure are thus rendered obvious. Nevertheless, if the spectrum observed at pressure 759·5 mm. and temperature 12°·7 C. be compared with that taken at 778 mm. and temperature 11°·5 C., it will be seen that there is a considerable difference between them, which may roughly be indicated by the former conditions yielding 55 measurable bands, while the latter gives only 36. This is not to be accounted for by a difference merely in the quantity of benzene in the tube, as the following statement will show:—

The calculated weight of benzene in 79 c.c., the capacity of the tube—

	° C.		mm.		grm.
At	11·5	and	778	=	0·0175
,,	12·7	,,	759·5	=	0·0184
,,	100	,,	757	=	0·2021
,,	100	,,	4	=	0·0011

The tube used for different pressures was not the same, although of the same length; that for different temperatures being of glass, there may have been some reflection from the inner surface by which the absorption bands would be rendered less distinct, and this most probably is partly, if not entirely, the cause of the differences in the two series of spectra.

In the examination of other aromatic hydrocarbons the bronze tube was used, and such differences do not occur.

On the tabulated statement the wave-lengths of the bands measured by Pauer, Friederichs, and Grebe, are quoted for comparison.

The accuracy of the measurements compares favourably with those made by Friederichs and by Grebe, who employed a small concave grating of 1 metre radius, because, as I have previously shown, the separation of the lines of different refrangibilities, with a quartz spectrograph having only one Cornu's prism of 60° C., is very great in the ultra-violet, when the quartz lenses are not achromatised. The standard lines of reference were the wave-lengths of the cadmium spark spectrum determined by Eder and Valenta.

There is evidence that the differences in the measurements of the bands in the different spectra observed by them are not due to inaccuracies, but to actual differences in the positions, or in the width of the bands; this arises from the different temperatures and pressures at which the several observations were made. Much more careful attention to atmospheric pressure and temperature becomes necessary when prolonged exposures extending from 1½ to 24 hours are made than when the period is only two minutes, but even under the latter conditions it is important.

On examining the various plates of spectra it was at once observed that, as the temperature rises, the bands which lie at the less refrangible end between λλ 2650 and 2700 (see Plates 32 and 33, figs. 1 and 5) become sharper and more intense; at the same time the bands in the more refrangible rays between λλ 2300 and 2500 become feeble, but this is because they are merged in a general absorption which weakens the emission spectrum. Pairs of bands in the less refrangible rays, which are so weak as to be barely visible at 25° C., become well defined and strong at 43° C. and 53° C. For examples, take the following. The measurements are recorded on each side of the bands when they are distinctly visible; the stronger edge of a group of bands is indicated by the thickened line of the angle.

At *t*	A band visible.	Only just visible.
12°·7 C.	╱2670 ⎸ 2672	— 2631

At *t*	A band, sharp and strong.	A faint band.	A band just visible.
25° C.	╱2670 ⎸ 2672	╱2661 ⎸ 2664	╱2625 ⎸ 2631

At *t*	A strong band.	A faint band.	A faint band.	A faint band.
43° C.	/2669 │ 2672	/2660 │ 2663	/2629 │ 2631	2625 —

At *t*	Four strong and well-defined bands.			
53 °C.	/2669 │ 2672	/2661 │ 2663	2631 —	/2625 │ 2626

There are likewise four feeble bands between wave-lengths 2260 and 2300, of which only one or two are visible at temperatures below 53° C.

The spectrum at 11°·5 C. and 21 mm. pressure is comparable with that at 12°·7 C. and 759·5 mm. bar. As the pressures increase, the temperature being constantly the same, gradual changes occur, as are seen, at constant pressure and increased temperatures up to 53° C. (Figs. 3 and 4, from 591 mm. to 88 mm., and from 67·5 mm. to 28·5 mm. pressure.)

Grebe observed a regularity in the differences between the wave-length of the bands, and he arranged them in twelve groups, seven of which are complete, and similarly constituted in that they contain in each group six bands. Of the five other groups, one contains five bands, and the others four in each group. An arrangement similar to that of Grebe fails to show such a relationship between the more numerous bands which I photographed ; nevertheless, the very appearance of the photographs affords evidence of great regularity in their arrangement in similarly constituted groups of bands, which are separated by similar intervals. The reason of this is quite intelligible when the changes in each band and in the constitution of the groups brought about by changes of temperature are closely examined. The first group lies, for instance, between λλ 2589 and 2650 ; then there is an isolated band—or possibly it is a feeble narrow group—about λ 2670. The next group lies between λλ 2528 and 2560, the third between λλ 2469 and 2500, the fourth between λλ 2416 and 2430, the fifth between λλ 2365 and 2380, or thereabouts, but the termination is difficult to see, because of the general absorption which renders the last band less distinct. These groups, which were measured at 12°·7 C., are seen to be composed principally of a very strong band and one narrow and less strong, which order is repeated generally four times in the same group, then a weak band is seen lying close to the strongest, but on the more refrangible side. (See fig. 1, about λ 2540, at temperatures about 12°·7 C. to 53° C.) The bands diminish in intensity as the refrangibility decreases. The groups of vapour bands appear to be caused by the overlapping of two or more similarly constituted spectra differing in intensity. The bands described as strong which fall within this description number fifty-four, there being twenty-seven in each of the two spectra. In addition to these there are thirty feeble bands, which also fall into two series of similar groupings, but with less regularity. To render this evident they have all been mapped according to a scale of inverse wave-lengths, or oscillation frequencies, with the result that the entire number of bands observed between the limits of 12°·7 C. and 25° C., under a pressure of 759·5 mm., is resolved into four spectra (see map, p. 484), of which two are strong and two are weak.

The Spectrum of Toluene.

The specimen of toluene was obtained from Kahlbaum. It boiled with no variation at 111° C., with the barometer at 763 mm. Rise of temperature from 10° C. to 90° C. has very little effect upon the toluene spectrum (see fig. 5), that is to say, the constitution of the groups of bands in rays less refrangible than λ 2400 is scarcely altered, and the number of bands is not increased, they only widen, but the general absorption of the more refrangible rays increases, and the change is decidedly greater at 100° C. Variations in pressure at 11° C. likewise scarcely affect the bands (see fig. 6), but the alteration is chiefly in the rays more refrangible than λ 2300. It is very remarkable that the series of bands and their particular grouping, which is characteristic of the benzene molecule, is greatly modified by the very simple substitution of CH_3 for H. It was remarked by Grebe that the spectrum is quite different from that of benzene, but on careful observation of the different temperatures and pressures at which benzene and toluene have been photographed this is seen to be not quite correct. The different temperatures at which the spectra were photographed were 10°, 30°, 40°, 50°, 60°, 70°, 80°, 90°, and 100° C. (fig. 5), with a barometric pressure of 751 mm. This series shows to perfection that the general absorption gradually increases with the temperature. There is a very feeble absorption of the continuous rays by toluene at all pressures, the last line of cadmium, λ 2144, being quite cut off, and all lines more refrangible than wave-length 2471 are weakened.

The following grouping of the toluene bands shows every band measured from that substance. The numbers in brackets represent six bands observed by Grebe which do not appear on my photographs :—

I.	II.	III.	IV.	V.	VI.
2695	—	—	—	—	—
44	2689	—	—	—	—
2651	43	2687	—	—	—
29	2646	45	2682	—	—
2622	29	2642	45	2674	—
20	2617	26	2637	41	2670
2602	18	2616	26	2633	39
31	2599	22	2611	27	2631
2571	31	2594	21	2606	27
30	2568	36	2590	18	2604
2541	38	(*2558*) ?	—	(*2588*) ?	—
35	2530	37	—	35	—
(*2506*) ?	38	(*2521*) ?	—	2553	—
83	2492	40	—	—	—
(*2423*) ?	75	(*2481*) ?	—	—	—
48	2417	70	2471	—	—
2375	58	2411	63	—	—
—	2359	58	2408	—	—
—	—	2353	59	2397	—
—	—	—	2349	—	2391

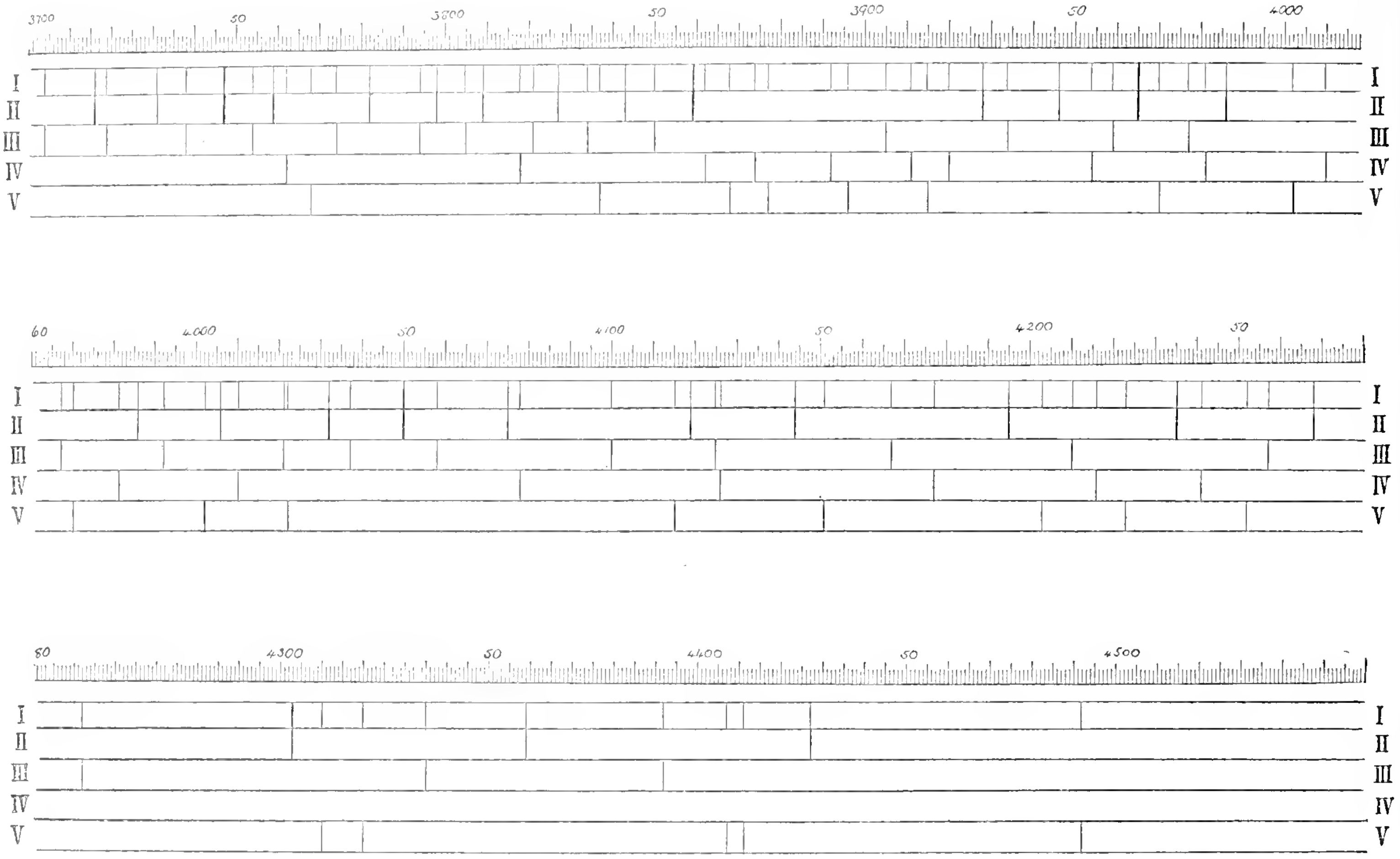
A regularity is apparent in the differences between the wave-lengths of the successive bands in the six different groups.

On the Relationship between the Bands of Benzene and Toluene.

It will be seen on comparing their measurements that, without being precisely similar, all the bands of toluene have corresponding bands in the benzene spectrum. Where the former are weak and the latter strong it might be supposed that a trace of benzene was contained in the toluene, but where both groups of bands are strong it is evident that they are common to both spectra, even when the bands show slight differences between the values of their wave-lengths. The principal difference lies in the most important groups of bands in the toluene spectrum being situated more in the direction of the red rays than the corresponding groups in benzene, but notwithstanding this shift of the bands to a less refrangible region which had long previously been observed in the spectra of solutions, a similarity in constitution is to be seen between certain groups of bands in toluene and others in benzene. Furthermore, both spectra have one very strong band in common; though this is best shown on the photographs, a tabulated statement of the measurements of the spectra also makes it apparent. The bands of toluene appear generally in pairs of similar intensity, while those of benzene are composed, as already stated, of one strong band and one slightly less strong. The pairs of the toluene bands diminish in intensity as they lie more towards the more refrangible rays, and if the individual narrow bands were brought closer together they would constitute a group scarcely distinguishable from one of the benzene groups. This suggests that the same vibratory motions are taking place

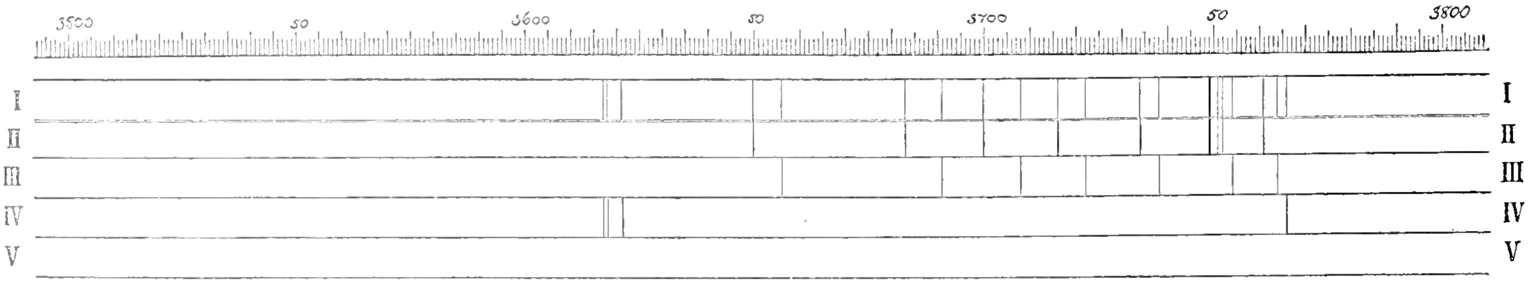
MAP OF ABSORPTION BANDS.

The Absorption Spectrum of Benzene Vapour Drawn to a Scale of Oscillation Frequencies and the Bands Divided into Four Series.



I. The whole spectrum.
II. First series, strong bands.
III. Second series, strong bands.
IV. Third series, weak bands.
V. Fourth series, weak bands.

The Absorption Bands in the Least Refrangible Rays Observed at Reduced Pressures varying from 206 mm. to 37 mm. at a temperature of 100° C.



within the benzene and the toluene molecules, but as the bands of toluene are shifted into rays of longer wave-length, or less oscillating frequency, and are more widely separated, this effect must be attributed to the weighting of the molecule by the addition of CH_2 to the benzene. To compare the spectra properly, benzene at 50° C. and toluene at 80° C. should be chosen, since both substances at these temperatures are 30° C. below their boiling-points.

GREBE has compared the ethylbenzene spectrum with that of toluene and found the bands of the one to be contained in the other.

The Homologues of Benzene and Toluene.

The principal homologues of benzene and toluene* were studied and their spectra measured and compared. The hydrocarbons were obtained on different occasions from Kahlbaum and were found to have the correct boiling-points. They were redistilled and their boiling-points taken immediately before being used. The following is a list of these substances. Their boiling-points were constant:—

		° C.		mm. bar.
Ethylbenzene	boiling-point	136·5	at	766.
Dimethylbenzenes, or *xylenes*—				
1 : 2 or *ortho*	,,	144	,,	763.
1 : 3 ,, *meta*	,,	138	,,	765.
1 : 4 ,, *para*	,,	138·5	,,	765.
Methyl-propyl benzene 1 : 4, or cymene	,,	177	,,	769.
Trimethylbenzene 1 : 3 : 5, or mesitylene	,,	165	,,	758.

The leading features of the three xylenes, cymene, and mesitylene, at different temperatures and constant pressure, are spectra with comparatively few bands or groups of bands; they have not been reproduced and therefore a detailed description of the photographs is given. They are each distinguished by a most powerful absorption of all rays at elevated temperatures, extending from about λλ 2800 to 2340, but on lowering the temperature the rays between these limits are transmitted, at first only feebly, and more strongly subsequently. The highest temperatures at which the substances were examined are described first in each case.

Description of the Spectra.

Ortho-xylene vapour. (Table XII., p. 512.)

At 121° C.—Complete absorption commences abruptly at approximately λ 2800, which is so intense that the strong cadmium lines are extinguished. This absorption

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[*] See also PAUER, 'WIEDEMANN'S Ann.,' 1897, 61, pp. 363–379; W. FRIEDERICHS, 'Zeitschr. f. Wissenschaftl. Photogr.,' 1905, vol. 3, p. 154; L. GREBE, *loc. cit.*, 1905, p. 363.

is continuous to about λ 2340. The three lines Cd λλ 2329, 2318·8, and 2288 are feebly transmitted.

At 100° C.—There is a sharp abrupt absorption commencing at λ 2748, which is complete until the group of lines λλ 2329 to 2265 is reached, and these are transmitted.

At 72° C.—The same absorption occurs, but is not abrupt and not so intense. The rays are feebly transmitted near λλ 2748, 2575, and as far as λ 2329.

At 45° C.—There is a complete, but feeble, transmission of all rays as far as λλ 2329, 2234·9.

At 20° C.—The same, but stronger, extending to λ 2194·7, which is feeble. A feeble band is seen near λ 2700.

Meta-xylene vapour. (Table XIII., p. 513.)

At 100° C.—There is almost a complete absorption which is not abrupt, from λλ 2700 to about 2350. Rays are transmitted from λλ 2350 to 2234.

At 70° C.—The rays are feebly transmitted from λλ 2680 to 2234, but a broad and weak band extends from λλ 2600 to 2500.

At 40° C.—The rays are well transmitted to λ 2194·7, but they are crossed by 12 groups of absorption bands.

At 11° C.—The rays are well transmitted, but with fewer bands.

Para-xylene vapour. (Table XIV., p. 514.)

At 100° C.—The spectrum is transmitted as far as λ 2802; beyond λ 2794 there is complete absorption to λ 2350. Bands are seen at λλ 2802 and 2800. Rays are transmitted at λ 2288.

At 70° C.—The same, but the bands are more distinctly visible.

At 40° C.—The spectrum is transmitted, except where the bands occur, as far as λ 2334·9.

At 10° C.—A similar spectrum, with the bands more conspicuous.

On comparing the spectra of the three xylenes (dimethylbenzenes) with that of benzene by inspection of the original photographs, the greatest similarity is seen between the *meta*-xylene and benzene in so far as the grouping of the bands is concerned, and the positions in which they are situated. There is also the fact that the bands in *meta*-xylene are well defined, like those of benzene. Some of the bands which are apparently common to the two substances are much reduced in width in *meta*-xylene, as, for instance, those at λλ 2609 and 2606, and those bands in the spectrum of *meta*-xylene which lie between λλ 2748·7 and 2575 fuse, or merge into one another rapidly as the temperature rises, and are rendered indistinct by an increasing general absorption. The correspondence of the one spectrum with the other is best seen by superposing one on the other; the groups are then easily identified.

Para-xylene has a spectrum which differs to some extent in constitution from that of *meta*-xylene. The groups of bands are situated in the same region as those in the *meta*-xylene; but bands appear in the *para*- at low temperatures which are seen only at higher temperatures in the *meta*-derivative.

The *para*-xylene shows a number of bands in the less refrangible region at higher temperatures which do not appear at all in the *meta*-xylene spectrum. In character the bands are more diffuse than in the *meta*-xylene, and not so sharply defined.

Ortho-xylene has an absorption spectrum which contains groups of bands similar to those in the *meta*- and *para*-isomers, but they are much more diffuse, and at first sight the spectrum bears but a slight resemblance to that of benzene.

Thus the similarity between the spectra of *ortho*-, *meta*-, and *para*-xylene and that of benzene is greatest with *meta*-xylene; it decreases with *para*-xylene, and is decidedly the least in the case of *ortho*-xylene. From the chemical point of view of position isomerism it is not easy to account for this difference, since it would rather be expected that either the *ortho*- or the *para*-xylene would most nearly resemble the ethylbenzene or toluene.

Ethylbenzene has a spectrum closely resembling that of benzene, and it occupies a position between toluene and *meta*-xylene, which is its natural position.

The spectra of ethylbenzene and toluene are almost identical, both as regards the number of bands and their wave-length; where a difference in wave-length occurs, the band in the ethylbenzene spectrum is generally somewhat shifted more towards the red than the corresponding toluene band, which again is to be attributed to the weighting of the molecule. Tables X. and XI., pp. 510, 511.

Ethylbenzene shows a much greater similarity to toluene than toluene does to benzene, the substitution of CH_3 for H in the side chain producing but a slight alteration in the spectrum.

A Comparison of the Absorption Spectra of the same Quantity of Benzene Vapour under Different Conditions as to Temperature and Pressure.

Photographic plate I., spectrum 1, fig. 1. (See Plate 32.)

The spectrum is produced by 0·0179 grm. of benzene at 12°·7 C. and 53 mm. of pressure.

Photographic plate III., spectrum 2. Not reproduced.

This is produced by 0·0179 grm. of benzene at 100° C. and 69 mm. pressure.

The two spectra differ widely; at 12°·7 C. the spectrum is divided into groups of well-defined absorption bands which extend through the region lying between wave-lengths 2700 and 2250. At 100° C. the positions of the different groups are still well defined, but the individual bands of the groups cannot be clearly distinguished, by reason of a general absorption overlying that portion of the photograph where the bands are seen to be the strongest at the lower temperature of 12°·7 C.

In addition to this change, a very strong and well-defined group of bands comes out clearly at the less refrangible end below wave-length 2575. These are seen in fig. 4 at 67·5 mm. and 22·5 mm. pressure and 100° C. Only the strongest band of this group appears at 12°·7 C. The principal differences observed between the benzene spectra at low and high temperatures with varying pressures may be summed up as follows:—At 100° C. the same quantity of benzene vapour produces greatly increased general absorption, extending over that part of the spectrum in which the groups of bands occur. At 100° C. the characteristic absorption is greatly increased at the less refrangible end of the spectrum, giving rise to a strong and well-defined series of bands, of which previously there had been only rudimentary indications. At 100° C. the bands have a peculiar sharpness, particularly those of the series less refrangible than wave-length 2575.

Benzene. (Fig. 1.)

The numbers of bands observed in the spectra at 759·5 mm. bar. and different temperatures, in a glass tube:—

° C.	Bands.	
At 12·7	55	
,, 25·0	84	
,, 43·0	82	The increased general absorption decreases the number of bands.
,, 53·0	56	

The numbers of bands observed at 11°·5 C. and different pressures, in a brass tube:—

(Fig. 2.)

mm.	Bands.
At 778	36
,, 483	38
,, 253	46
,, 21	44

The numbers of bands observed in the spectra at 100° C. and at different pressures:—

(*Not reproduced.*)

	mm.	Bands.	
Photographic plate I., No. 13.	At 683	9	A general absorption extinguishes many of the bands. There is a gradual increase, principally at the less refrangible end, in the number of bands on reduction of pressure.
	,, 589	13	
	,, 478	14	
	,, 381	16	
	,, 279	17	
	,, 172	18	

(Fig. 3.)

	mm.	Bands.	
Photographic plate II., No. 14.	At 767	5	A great general absorption extinguishes nearly all the bands, then a gradual increase in their number follows on reduction of pressure, the increase being at the less refrangible end of the spectrum.
	,, 591	9	
	,, 484	9	
	,, 332	12	
	,, 206	13	
	,, 142	11	
	,, 99	14	
	,, 88	15	

At 100° C. and different pressures :—

(*Not reproduced.*)

	mm.	Bands.	
Photographic plate III., No. 15.	At 92	25	At these reduced pressures there is a large increase in the number of bands; the principal groups of bands are all visible.
	,, 69	36	
	,, 43	50	

(Fig. 4.)

	mm.	Bands.	
Photographic plate IV., No. 16.	At 67·5	31	The barometer stood at 757 mm. There is a large and regular increase in the number of the bands on reduction of pressure as far as 15·5 mm. The effect of the general absorption and of the selective absorption is well seen. There is at pressures varying from 9 mm. to 4 mm. a gradual decrease in the number of bands on reduction of pressure, because, although the bands in the centre of the spectrum are visible, those at the less refrangible end, which at 767 mm. pressure are well seen, do not now appear, the quantity of substance being insufficient. In fact, there is at first a shifting of the general absorption towards the less refrangible rays, and subsequently the bands seen at this end are extinguished. The regularity in the variation of the spectra is obvious on photographic plates II. and IV. (Nos. 14 and 16).
	,, 52·5	54	
	,, 37·5	60	
	,, 28·5	72	
	,, 22·5	75	
	,, 15·5	88	
	,, 9·0	52	
	,, 5·0	38	
	,, 4·0	30	

In conclusion I have much pleasure in acknowledging the great care with which my assistant, Mr. A. G. G. Leonard, A.R.C.Sc.I., has photographed and accurately measured all of the vapour spectra of benzene and its homologues under different conditions, and the precise account he has rendered of the numerous analyses of the vapours, which were performed in different ways.

TABLE I.—Absorption Bands in the Spectrum of Benzene Vapour at Different Temperatures and a Barometric Pressure of 759·5 mm.

Abbreviations:—s., strong; f., feeble; n., narrow; v.s., very strong; b., broad.

Well-marked groups of bands are indicated by /——— in the first column.

Similar bands, or groups, are indicated by the same Greek letters.

	12°·7 C. λ.	25° C. λ.	43° C. λ.	53° C. λ.	References.* λ.	
		2745 f.	2741 f.	2744 f.		
		40 f.	32 f.			
		36 f.	09 f.			
		2694 f.	2695 f.	2695 } f.	2694 F.	
				92 }		
		89 f.	89 f.	89 } f.	89 G.	
				88 }	88 F.	
				83 }	84 G.	
			81 f.	80 }	81 F.	FRIEDERICHS' 1st group.
	2678 }		78 }	78 }	78 G.	
	76 }	76 f.	75 }	75 }	75 F., 76 G.	
α	72 }	72 } s.	72 } s.	72 } s.	71 G.	
	70 }	69 }	69 }	69 }	70 G. F. & P.	
		66	67 } f.	67 } f.		
		64	64 }	64 }	65 G.	
		61 } f.	63 } f.	63 } s.		
		60 }	60 }	61 }	61 F.	
		58 f.		58 f.	59 G.	
		54 f.	55 v.f.		55 G.	
		50 f.	50	48	49 G.	
		45 f.	47 } f.	46	45 G.	FRIEDERICHS' 2nd group.
			44 }		43 G.	
	39 f.	39 f.	39 f.	40 } f.		
	36 f.	36 f.	37 f	37 }	38 F.	
β			36 f.	36 } f.	37 G.	
	34 f.		33 f.n.	34 }	33 F. & G.	
	31	31	31 } f.	31 s.	31 F.	
		28	29 }	28 f.	28 G.	
			27 f.	26 } s.		FRIEDERICHS' 3rd group.
		25	25 f.	25 }	25 F. & G.	
	22 } s.	22	22 } f.	22 f.		
	}	21 }	21 }	20 } s.	20 G.	
	}	19 }	19	19 }		
	17 }	17	17 } s.b.	17 } s.b.		
	16 } s.		}	}		
γ	}	15 } s.	}	}	14 F. & G.	
	13 }	13 }	13 }	13 }	13 P.	
	12 } s.	12 } s.	11 } s.	11 } s.	10 P.	PAUER'S group I.
	08 }	08 }	08 }	08 }	09 G.	
	06	06	07 } s.	07 } s.	04 G.	
	05 } s.	05 } s.	}	}	03 F.	
	03 }	02 }	02 }	02 }	02 P.	

* P., PAUER; F., FRIEDERICHS; G., GREBE.

TABLE I. (continued).

	12°·7 C. λ.	25° C. λ.	43° C. λ.	53° C. λ.	References. λ.	
	2601 ⎫ s.					
	2599 ⎭	2599 ⎫ s.	2600 ⎫ s.	2600 ⎫ s.		
γ	97 ⎫ s.	97 ⎭	2597 ⎭	2597 ⎭	2598 F. & G.	
	93 ⎭					
		96 ⎫ s.b.	96 ⎫ s.	97 ⎫ s.		
	90	91 ⎭	91 ⎭	91 ⎭	93 P. F. & G.	
		89 f.	89 f.		88 F.	FRIEDERICHS' 4th group.
			85 f.	85 f.n.	87 G.	
				83 f.n.		
		81 f.	80 f.	81 f.		
				79 f.	78 G.	
	72	71 f.	71 ⎫ f.	72 ⎫	73 G.	
			70 ⎭	69 ⎭	70 F. & P.	
	65 ⎫	66 f.	67	67 f.	68 F., 66 G.	
	62 ⎭	62 f.	63 ⎫ s.	62	64 F., 63 G.	
	61 ⎫	60 f.	61 ⎭	59	61 F.	
	59 ⎭					
	58 ⎫ f.		60 ⎫ s.		58 G.	
		56 f.	57 ⎭			
	54 ⎭	54 f.	55	55	55 G.	
	53 ⎫ s.	53 ⎫ s.		54 ⎫		
	52 ⎭	52 ⎭	52 ⎫ s.	51 ⎭	53 G.	
δ			50 ⎭		50 F. & P.	PAUER'S group II.
	51 ⎫ b.	50 ⎫ s.b.	49 ⎫ s.b.			
	46 ⎭	47 ⎭	46 ⎭		47 G. & P.	
	43 n.	44 ⎫ s.b.	43 ⎫ s.b.		43 G. & F.	
	42 ⎫ s.	42 ⎭				
	40 ⎭		39 ⎭			
	38 ⎫	38 ⎫ s.b.	38 ⎫		38 F.	
	35 ⎭	34 ⎭	35 ⎭		37 G.	
	33 ⎫ s.b.	33 ⎫ s.b.	33 ⎫ s.b.		35 P., 34 G.	
	29 ⎭	29 ⎭	27 ⎭	27	30 F.	
	28	28 ⎫ s.			28 P.	
	27 ⎫ f.	26 ⎭			26 F. & G.	
		25 ⎫ f.	24 ⎫ s.b.	25 ⎫ s.		
	23 ⎭	22 ⎭	21 ⎭	22 ⎭		
		20 f.	20 ⎫ f.		20 G.	
			19 ⎭	19		
	16 ⎫ f.	16 ⎫ s.	18 ⎫ s.	17 ⎫	16 F.	
	13 ⎭	13 ⎭	12 ⎭	12 ⎭		FRIEDERICHS' 5th group.
	12 ⎫ f.		11 ⎫ f.		11 G.	
	09 ⎭	08 f.	09 ⎭	09	10 F. & P.	
			08 ⎫ f.		08 G.	
		06 f.	05 ⎭	06		
	01 f.	01 ⎫ f.	02 ⎫ f.	01 ⎫ b.v.f.		
	2499	2499 ⎭	2499 ⎭		00 F. & G.	
η		98 ⎫ f.	99 ⎫ s.			
				2496 ⎭	2497 P., 96 G.	
	96 n.	96 ⎭	97 ⎭			
			96 ⎫ s.		95 P.	
		94 ⎫ f.	94 ⎭	94	94 G.	
			93 ⎫ s.			
		91 ⎭		91		
	89 n.	91 ⎫ f.			89 G., 88 P.	PAUER'S group III.
	87	87 ⎭	87 ⎭			

Table I. (continued).

	12°·7 C. λ.	25° C. λ.	43° C. λ.	53° C. λ.	References. λ.	
		2486			2485 G.	
	2483					
		84 } b.	2484 } s.			
	82 } s.					
	81	80	79		81 F.	
	79	79 f.			79 G.	
θ	78 } s.		78 } f.		78 P.	
	77	77 f.				
			75			
	74 } s.b.	74 } b.	73 } f.		74 G., 72 P.	
	71	69	67		70 G. & F.	
	69 n.	69 n.			67 G. & P.	
	69 } f.					
	64	66	66 } s.		67 G. & P.	
		65	64		63 F. G. & P.	
	58 } f.	57 } s.	57 } s.	2457 } f.	58 F.	
	55	54	54	55	56 P.	
	53 f.		53 } f.		54 G.	
			51	52	51 F.	
			50 } f.			Friederichs' 6th group.
			47		48 G.	
	44 } f.	44 } f.b.	43 } b.		45 P.	Pauer's group IV.
	43	39	38		38 G., 40 P.	
		37 f.	36 f.		36 G.	
	33 } f.	33 f.				
	31					
		30 f.			30 F. & G.	
	29 } f.					
ι	27	28 f.	27 f.		27 P.	
	26 } f.				26 G. & F.	
	24	24 f.	24 f.		23 G., 25 P.	
	20 } f.b.	20 f.	20 f.		20 F. & P.	
	18	18 } f.b.			19 G.	
	17 } s.		17 } b.			
	16				15 F.	
	15 f.	13	13			
	13 } f.	11 f.	11 } f.		12 G. & P.	
	09	10 f.	09	09 f.	08 F. & G.	
	02	03 } f.	03 } s.	03 f.	04 F.	
		00	00		00 G. & P.	
			2398 f.		2397 F.	
		2394 f.	94 f.	2395	94 G.	
κ		86 v.f.	91 f.		92 G.	
		85 v.f.	84 f.		88 F.	
		80 f.n.			81 F., 82 G.	
	2379 f.n.		77 f.		78 G., 77 P.	
	76	75 f.				
		73 f.			73 G.	Friederichs' 7th group.
			72 f.			
		69	68		70 G. & F.	
	65	64 } f.	65 } f.		62 P.	
		62	61		60 G.	
		58	58 f.		56 F., 57 G.	
		52				

TABLE I. (continued).

	12°·7 C. λ.	25° C. λ.	43° C. λ.	53° C. λ.	References. λ.	
			2349 v.f.		2347 G., 46 F.	
		2343	43 v.f.			
			42 f.		41 G., 37 F.	
			30	2330		FRIEDERICHS' 8th group.
		24	24 s.	25	28 F.	
				20	19 F.	
		08	07	15	08 F.	
			05	07	05 F.	
			2294	2295		
		2277		77		
				69	2270 F.	FRIEDERICHS' 9th group.*
			59	67	59 F.	
	2226			†		
	55 bands	84 bands	82 bands	56 bands		

* In KAYSER'S 'Handbuch der Spectroscopie,' vol. III., p. 368, these bands are given as the beginnings of a probable 9th group.

† On the photographs several distinct and well-defined bands are seen here, but under the microscope they are too indistinct to be measured.

TABLE II.—Absorption Bands in the Spectrum of Benzene Vapour at 11°·5 C. and Different Pressures.

Abbreviations :—s., strong ; f., feeble ; n., narrow ; v.s., very strong ; b., broad.

	778 mm. λ.	483 mm. λ.	253 mm. λ.	21 mm. λ.		778 mm. λ (continued).	483 mm. λ (continued).	253 mm. λ (continued).	21 mm. λ (continued).
		2700 f.n.	2706 f.				2678*		2680*
		2695 } f.	2695 } f.			2676 f.	76 n.	78 }	78 }
		91	91	2691 n.			75 n.	75	75
		90 }	90	89 n.	α				75*
		88	85			71 } s.	71 } s.b.	71 } s.	71 } s.
		81 } f.	83 } f.	82 }		69	69	69	69
		78	80	80			67		

* A very narrow distinct band at each of these positions lies so close to the next band as not to be distinctly measureable. See pp. 478, 479.

TABLE II. (continued).

	778 mm. λ.	483 mm. λ.	253 mm. λ.	21 mm. λ.
		} f.		
		2666 }		2666 f.
	2663 } f.	63 } s.	61 } s.	61 }
	60 }	59 }	60 }	59 }
		58	53 f.n.	58
		51 } f.	51 f.n.	51 } f.
		47 }		47 }
				47 } f.
		44 f.		44 }
		38 f.	40 }	
		36 f.	35 }	39 }
				37 }
				36 }
β			34 n.	34 }
		33 } f.		33 n.
		31 }	31 } s.	31 }
		30	29 }	30 }
		26 }	28 } s.	28 } f.
		25 }	25 }	25 }
				23 } f.
		22 n.		22 }
	21 }		21 } s.	21 } s.
	19 }	19 }	19 }	19 }
	18 n.	18 }	18 } s.b.	17 }
	16 } b.	17 } s.b.		16 }
				15 } s.
	13 }	12 }	13 }	13 }
γ	11 }	11 } s.b.	12 } s.b.	11 } s.
	08 }	08 }	08 }	08 }
	07 } s.b.	07 } s.b.	08 } s.	07 } s.b.
	02 }	02 }	02 }	02 }
	01 } s.b.	00 } s.b.	01 } s.	00 } s.
	2598 }	2597 }	2597 }	2597 }
	97 } s.b.	97 } s.b.	97 } s.	96 } s.
	91 }	91 }	91 }	91 }
		90 } f.	89 n.	88
		87 }		
	*87 } f.	87 } f.		
	87 }	85 }	85 n.	85
		84 } f.		
		82 }	82 n.	82
		81		77
	71	71 } s.b.	72 } s.	71 } s.
		69 }	71 }	70 }
	68	68 } f.		69 } f.
		67 }		67 }
	62 n.	63 } f.	63	65 } f.
	61 n.	62 }	62	62 }
			60	60
	59 } f.b.		56 n.	55
	55 }			
	53 } b.		52 n.	
	50 }		49 n.	

	778 mm. λ (continued).	483 mm. λ (continued).	253 mm. λ (continued).	21 mm. λ (continued).
	2549 } f.b.		2547 n.	
	45 }			
δ	44 } f.b.	43 }	44 n.	
		40 }		
	39 }			
	38 } f.b.			
	34 }			
	30 } f.b.	30		
		29 }		
	27 }		27	27
		26 }		
	25 } f.			
		24 }	24 } s.	24 }
	22 }		22 }	22 }
		21 }		21 } b.
			19	19 }
	16 } f.			18 } s.
		15 }	14 } s.	16 }
	13 }		13 }	
		11 }	11 } f.	
		10 } f.		09
η	08	08 }	07 }	
			07 } f.	07
	01		06 }	
	2496		2497	
	93 } v.f.			
	88 }			
	85 } f.			
	81 }			
θ	79 } f.			
	77 }			
	75 } f.			
			72 } b.	
	70 }			
			69 }	
	68 } f.		67 } b.	
	64 }		64 }	
	58 } f.		58 } b.	
ι	55 }		55 }	
	18 } f.		07 } b.	
	13 }		05 }	
	2377			
κ	25			
				2334 n.f.
				26
			2295 n.	24
			79	
			68	
		2277		2277
	36 bands	39 bands	46 bands	44 bands

TABLE III.—The Absorption Spectrum of Benzene Vapour, at 100° C. and Different Pressures, in a Column 150 mm. long.

Abbreviations :—f., feeble ; s., strong ; r.s., rather strong ; v.s., very strong ; n., narrow ; b., broad ; v.n., very narrow ; n.s., narrow, strong.

(Photographic Plate No. 1, 1906–7.)

683 mm. λ.		589 mm. λ.		478 mm. λ.		381 mm. λ.		279 mm. λ.		172 mm. λ.	
2743	f.	2741·5	f.	2719	r.s.	2719	f.	2717	v.f.	2703·5	f.
41		40		16		15		12	v.f.	00·5	f.
39	f.	38	f.	13	f.	12	s.	06	r.s.	2698	
36		19	r.s.	09·5		09·5		03		94	s.
26	f.	15		05·5	s.	05	s.	01	r.s.	91	
15		13	r.s.	03		03		2699		90	s.
14	f.	09		01·5	s.	00	s.	96	s.	86	
09		06	s.	2699		2697·5		92		82	v.s.
08	r.s.	03		96	s.	96	s.	90	s.	79	
03		00·5	s.	94		91		87		78	s.
02	r.s.	2697·5		91	s.	89	s.	84	v.s.	75	
2698		96	s.	88		87		80		72	s.
96	r.s.	91		85	s.	84	s.	78	s.	69	
91		90	s.	80		79		75		66	f.n.
90	r.s.	87		78	s.	78	s.	72	s.	65	f.n.
87		84·5	s.	75		75		68·5		62	v.s.
84	r.s.	79		73	s.	73	s.	66	n.s.	59·5	
79		78	s.	69		68		65	n.f.	58	f.n.
		75		66	n.s.	66	n.s.	63	v.s.	54	f.n.
		73	s.	65·5	v.n.	65	v.n.	59		52	f.n.
		68		63	s.	63·5	v.n.	58	f.n.	48	f.
		66	n.s.	59·5		62	s.	56	f.n.	44·5	f.
		64	f.	58	f.n.	59		2284·5	b.f.	2284	b.f.
		59·5		2277·5	f.	58	s.	77·5	s.	75·5	s.
				75		57		75		75	
						55	f.n.	74	f.n.	74	n.f.
						2277·5	f.				
						75					
9 bands		13 bands		14 bands		16 bands		17 bands		18 bands	

TABLE IV.—The Absorption Spectrum of Benzene Vapour, at 100° C. in a Column 150 mm. long, at Different Pressures.

Abbreviations:—f., feeble; s., strong; n., narrow; n.f., narrow, feeble; n.s., narrow, strong; r.s., rather strong; v.f., very feeble; f.n., feeble, narrow.

(Photographic Plate No. 2, 1906–7.)

767 mm. λ.		591 mm. λ.		484 mm. λ.		332 mm. λ.		206 mm. λ.		142 mm. λ.		99 mm. λ.		88 mm. λ.	
2761	f.	2761	f.	2741	n.	2741	f.	2718	v.f.	2706	s.	2706	s.	2706	f.
57		57·5		40	n.	39		15		03		03		02	
56	f.	54	f.	19	f.	18	f.	13	v.f.	2699·5	s.	00	s.	00	r.s.
56		40	n.s.	15·5		14·5		09		97		2697		2697	
40·5	n.f.	39	n.s.	13	f.	13	f.	06	r.s.	94	s.	94	s.	94	s.
40	n.	38	f.	09·5		09		03		90		90		90	
37	f.	35		06	r.s.	06	r.s.	00	s.	88	s.	89	s.	88	s.
35		18	f.	03		03		2697		85		85		85	
		14		00	r.s.	00	s.	95	s.	83	s.	82·5	s.	82	s.
		13	f.	2697		2697·5		91		79		79		78	
		08		96	r.s.	96	s.	89	s.	78	s.	77	s.	77	s.
		07	f.	91		90		86		74		74		73·5	
		02		89·5	r.s.	89	s.	83·5	s.	71·5	s.	71	s.	71	s.
		01	f.	87		85·5		78		67		66		67·5	
		2697		83	f.	83·5	s.	77	s.	64	n.f.	64	n.f.	64	f.n.
				79·5		78		74		62	n.f.	62	n.f.	62	f.n.
						77	f.	72	s.	60	s.	60	s.	59	s.
						74		67		57·5		57		57	
						70	f.	64	n.f.	56	f.	56	v.f.	56	f.
						66		63·5	n.f.			53·5	v.f.	53	v.f.
						64	f.	60	s.			51	v.f.	52	v.f.
						59·5	f.	58				2275	f.	46	v.f.
								56	f.					2275	f.
5 bands		9 bands		9 bands		12 bands		13 bands		11 bands		14 bands		15 bands	

Table V.—The Absorption Spectrum of Benzene Vapour, at 100° C. and at Different Pressures, in a Column 150 mm. long.

Abbreviations:—f., feeble; n., narrow; n.f., narrow, feeble; s., strong; v.f., very feeble; v.s., very strong; r.s., rather strong.

(Photographic Plate No. 3, 1906–07.)

92 mm. λ.		69 mm. λ.		43 mm. λ.		92 mm. λ.	69 mm. λ (continued).		43 mm. λ (continued).	
2704	f.	2706	v.f.	2700·5	f.		2598	f.	2569·5	n.f.
03		03		2697			94		66	n.f.
00·5	f.	01	f.	96	f.		93·5	f.	64	f.
2698		2698		94			88		60	
95	r.s.	95	f.	89	f.		86	n.f.	59	f.
92		91		86·5			83	n.f.	55	
89	r.s.	89·5	f.	83·5	f.		79·5	n.f.	28·5	f.
86		87		81			76·5	f.	27	r.s.
82	s.	82·5	f.	77	f.		70	s.	25·5	
80		80·5		74			68		24	f.
77	r.s.	77	r.s.	71	s.		67	f.	21	
75		74		68			2325	s.	20	f.
71	v.s.	70	v.s.	65	n.f.		24		19	
69		68·5		63	n.f.		2298	v.f.	16	f.
66	n.f.	65	n.f.	60	f.		94		12	
61	v.s.	62	n.f.	58			77·5	s.	09	f.n.
59·5		59·5	r.s.	37	f.		76		2468	f.
58	n.f.	58		34					66·5	r.s.
55	n.f.	56	n.f.	33	f.				64	
53	n.f.	54	n.f.	32					57	r.s.
48	n.f.	52	n.f.	28	r.s.				54·5	
46	f.	48	n.f.	26					52·5	f.
42		37	r.s.	25	f.				52	
39	f.	35		24·5					13	f.
34		34	r.s.	23	f.				12	
2591	n.f.	32		21					11	f.
87·5	n.f.	30·5	f.	19	f.				09	
85	n.f.	28·5		17	s.				03	f.
83	n.f.	28	r.s.	16					2386·5	f.
78	n.f.	26		15	s.				82	
2324	v.f.	25		10					77	r.s.
00·5	v.f.	24		09	s.				75	
2295	v.f.	23		05					74	f.
85	f.	21		04	s.				72·5	
80		19	n.	2599					69	
77	f.	18·5	f.	97·5	s.				67	
		16		94					61	
		14	f.	93	s.				25	r.s.
		10		88					24	
		09	f.	85·5	n.f.				2277·5	f.
		05		83	n.f.					
		02	f.	78	n.f.					
25 bands		2599·5		77	n.f.		36 bands		50 bands	

Table VI.—Absorption Bands of Benzene Vapour, in a

Abbreviations :—s., strong ; v.s., very strong ; r.s., rather

(Photographic

67·5 mm. λ.		52·5 mm. λ.		37·5 mm. λ.		28·5 mm. λ.		22·5 mm. λ.	
2706	f.	2706	f.	2706	f.	2703	v.f.	2701	v.f.
03		02		03		2700	v.f.		
00	f.	00	f.	01	f.				
2697		2697·5		2698					
95	r.s.	95	f.	96	f.	2694·5	r.s.	2694	v.f.
91		91		92·5		91			
90	r.s.	89	r.s.	90	f.	89	r.s.	88	f.
87		87		87		86		77	f.
82·5	r.s.	83	r.s.	84	f.	84	v.f.		
81		80·5		81		81			
77	r.s.	77	r.s.	78	r.s.	77	r.s.		
74		74		74		75		71	s.
71	v.s.	71	v.s.	71	v.s.	71	v.s.	69·5	
68		68		68·5		69		66	f.
65	f.	65	f.	68	v.f.	66	v.f.	65	f.
61	s.			65		64·5	v.f.	64	r.s.
58		60	s.	64	v.f.	62	s.	60	
		58		62		59·5		59	f.
56	f.n.			61	s.	58	v.f.	45	f.
		56	f.n.	59		48	v.f.	36	
				57·5	v.f.	47	v.f.	31	r.s.
				56		39	r.s.	29	r.s.
47	f.n.	49	f.	55	v.f.	37			
45	f.n.			52		36	r.s.		
43	f.n.	41		50	v.f.	35		25	r.s.
				46		33·5	r.s.		
37	r.s.	37	r.s.	38	f.	31·5		22	n.f.
35		35		37		30	r.s.	21	r.s.
34	r.s.	34	r.s.	36	f.	29·5		19	
32		32		33		28	r.s.	17	r.s.
31	r.s.	31	f.	31	f.	26	r.s.		
30		29		29·5		24		16	v.s.
28	r.s.	28	f.	28·5	r.s.	22	s.	13	
27		27		28		18		11	n.s.
26	f.	26	r.s.	26	r.s.	16	v.s.	10	v.s.
		24·5		25		12		08	
21·5		23	r.s.	24·5	r.s.	10	v.s.	06	v.s.
		22		22		07		05	
		19·5	r.s.	19·5	f.	06	v.s.	04·5	v.s.
		17		19	r.s.	01·5		02	
		16	f.	16·5				01	v.s.
		15		15	s.	00	v.s.		
		14	f.	11					
		11		10	s.	2597		2598	
		09·5	r.s.	05·5		96	v.s.	96	v.s.
		05·5		05		91		92	

Column of 150 mm., at 100° C. and Different Pressures.

strong; f., faint; v.f., very faint; n., narrow; b., broad.

Plate No. 4.)

15·5 mm. λ.		9 mm. λ.		5 mm. λ.		4 mm. λ.	
2703	f.						
02	f.						
2698							
97	f.						
94							
91	f.	2692	v.f.				
88		88	v.f.				
77	f.	78	v.f.				
76		75				2676	v.f.
72	s.	72	f.				
71		71					
70	s.	70	f.			70·5	n.f.
69		69		2669	n.v.f.	70	f.
67	v.f.	67	f.				
65	v.f.	66		66	n.v.f.	66	f.
64	r.s.	61	v.f.				
60		59	v.f.			47	v.f.
39	v.f.	39	f.				
36		36					
31	r.s.	34	f.				
30		33					
30	r.s.	31	f.				
28		30					
28	r.s.	29					
25		26	f.				
24	f.	25					
22		23	v.f.				
22	r.s.	22					
19·5		21	r.s.				
18	n.s.	19					
16·5	n.s.	17	n.r.s.				
16	s.	16	v.s.	16	s.	16	r.s.
13		13		12		13	
11·5	n.f.						
11	s.	11	s.	10	r.s.	10	r.s.
08		08		07		08	
07	s.	07	s.	06	r.s.	06	r.s.
05·5		05		04·5		05	
04·5	v.s.	04·5	v.s.	04	s.	04	s.
03		02		02		02	
01	r.s.						
00		00	s.	00	r.s.	00	s.
2599	s.					2597·5	
98		2597·5		2597			
96	v.s.	94·5	v.s.	94	v.s.	94·5	v.s.
91		91		91		91	

TABLE VI.

67·5 mm. λ.		52·5 mm. λ.		37·5 mm. λ.		28·5 mm. λ.		22·5 mm. λ.	
					s.				
		2605	r.s.	2599·5		2588	v.f.	2589	v.f.
		00		99	s.	85	v.f.	86	v.f.
		2598	f.	95		84	v.f.	82	v.f.
		95		97	s.	71	r.s.	71	f.
		94	f.	91		69		68	f.
				90	v.f.	69	r.s.	65	f.
		88		88		66·5		63·5	
2586	f.n.	87	n.f.	87	v.f.	65	s.	63	s.
85	f.n.	84	n.f.	85		61		61	
84	f.n.	79	n.f.	83	v.f.	59·5	r.s.	59	n.r.s.
80	s.n.	77	n.f.	81·5	f.	59	s.	59	s.
77	f.n.	70	r.s.	79		55		55·5	
		68		72	s.	54	s.	54	n.r.s.
		67	f.	71		50		53·5	s.
		65·5		69	r.s.	50	s.	51	
				67		46		50	s.
				65·5	r.s.	43	s.	46	
				62		40		44	s.
				59	r.s.			40	
				56					
						38	r.s.	38	s.
						35		35	
						33	r.s.	33	s.
				30	f.	29		29	
						28	s.	27	r.s.
				27		27		24	r.s.
		24	r.s.	24	r.s.	24	s.	22	
		22		22		21		21	f.
		20	f.	21	f.	19	r.s.	19	
		18·5		19·5		17	r.s.	16	s.
		16	f.	16	r.s.	14	s.	13	
		12		13		12		11	f.
				10	f.	11	s.	08	
						08		07	f.
						06·5	r.s.	06	
								04	f.
								02	
								01	s.
						00·5	r.s.		
						2498			
						98	f.	2496	
						96		94	s.
						93·5	f.	91	
						90		91	s.
								86·5	
						88	f.		
						85			
						83	f.	83	s.
						81		78	
						80	f.		
						79			
						78	f.		
						76		78	s.
						73		77	

(continued).

15·5 mm. λ.		9 mm. λ.		5 mm. λ.		4 mm. λ.	
		2565	r.s.				
2562	n.r.s.	62					
60	n.f.						
59·5	f.	59	r.s.	2557	f.	2559	f.
56		55		55		55	
54	n.f.	54	n.f.				
54	s.	52	s.	52	f.	52	r.s.
51		51		50		51	
50	n.f.	49·5	f.				
49	s.	49	s.	49	f.	49	r.s.
46		46		46		46·5	
45	s.					44	v.f.
43		43	s.			42	
42	s.	41	v.s.	41	s.	41	s.
40		40		39		40	
39	r.s.						
38		38	s.	37	s.	37·5	n.r.s.
36	r.s.	35·5	s.	35	r.s.	35	n.r.s.
35		35		34			
33	v.s.	33	v.s.	32	v.s.	32	v.s.
29		29		28		29	
27	n.f.	27	f.	27	f.	27	v.f.
25	f.						
22							
21	f.						
19							
18	f.	14·5	v.f.				
12·5		13					
12	f.						
08							
07	f.						
06							
04	f.						
02							
01	f.	01	f.	01	f.		
2499		2498·5	f.	2499			
97	f.			98	f.		
96		96		97			
93	f.	93	f.	96·5	f.		
91		91		95			
90	r.s.			94	v.f.		
89		89	f.	92			
88	r.s.	87	r.s.	91	v.f.	2487	n.f.
87				90			
84	s.	83	s.	89	v.f.	83	f.
82		81		87·5		82	s.
81	s.			86	n.r.s.		
80				83·5	r.s.	80	
79	n.r.s.	78·5	n.s.	82			
78	s.	77	s.	81	s.	77	n.f.
76		76		79			

TABLE VI.

67·5 mm. λ.	52·5 mm. λ.	37·5 mm. λ.	28·5 mm. λ.	22·5 mm. λ.
	2470 f.		2469 f.	2474 s.
				69
			68 r.s.	68·5 n.s.
	67	2467 f.	67 r.s.	
	66·5 f.	65	64	65 f.
	64	63 f.	58 r.s.	58 s.
	62 f.	61	54	54
	59	58 r.s.		
	57 f.	56		
	55			
			44 v.f.	45 s.
				39
				39 s.
				30
				28 s.
				26 s.
				24
				22 s.
				19·5
		18 f.	17 s.	18 v.s.
			13	15·5
		13		13 s.
		10·5 f.	09·5 f.	
			06 f.	
	03 f.	04 v.f.	04	03 r.s.
	2396 f.	02	03 f.	00
			01	2399 f.
				94
			2390 f.	91 f.
		2385 v.f.	86	86
			84 f.	85 f.
				83
				81 f.
				77
		77 v.f.		76·5 s.
			75 r.s.	75
		73 v.f.	73 r.s.	74 r.s.
			72	72
			70 r.s.	70 r.s.
2368·5 v.f.		67·5 r.s.	68·5	68
62	66 f.		65 s.	66 s.
		63	64	62·5
				62 f.

(continued).

15·5 mm. λ.		9 mm. λ.		5 mm. λ.		4 mm. λ.	
2473·5	v.s.	2475	v.s.	2477	s.	2472	s.
69		70		76		70	
68	n.r.s.			72	v.s.		
66·5	f.			69·5			
64·5							
57	f.	57	v.f.				
54		56					
54	f.						
52							
50	f.						
48							
45	f.						
40							
38	f.						
37							
36	f.						
33·5		31·5	v.f.	30	v.f.		
30	f.	29·5					
29	r.s.	29	v.f.	28·5		28	v.f.
27		26·5		28	v.f.	26·5	
26	r.s.	26	v.f.	26		26	v.f.
24·5		24		25·5	v.f.	24	
24·5	n.r.s.			24			
23							
22·5	r.s.	22	v.f.	22	v.f.	22	v.f.
21		19·5		19		19·5	
20	r.s.						
19							
18	v.s.	18	v.s.	17	v.s.	18	v.s.
15·5		15·5		15		15·5	
13·5	n.r.s.						
12	r.s.						
09							
07	v.f.						
04·5	v.f.						
01							
2396	v.f.						
90	v.f.						
89	f.						
87							
86	f.						
84							
82	f.						
81				2381	f.		
77·5	v.f.	2377	r.s.	79			
75·5	r.s.	75		78	f.		
75				77			
74	r.s.			76	r.s.		
72				75·5			
70	f.						
68·5							
66	r.s.	65	f.	64·5	f.b.	2365	v.f.
62		63					
60				59	f.		

Table VI.

67·5 mm. λ.		52·5 mm. λ.		37·5 mm. λ.		28·5 mm. λ.		22·5 mm. λ.	
				2361	r.s.	2360	f.	2360	f.
		2358	f.	58		58		58	
				58	r.s.	53	f.	54	f.
				56		49		49	
2354	v.f.	54	f.	54	b.r.s.	26	v.s.	25·5	s.
		49·5		49		24		24	
		46	f.	47	r.s.				
		43		44					
		40	f.	37	f.				
		37	f.	33·5				2277·5	r.s.
		34	f.	25·5	v.s.			77	
26	s.	26	s.	24		2266	r.s.		
24		24·5		03	v.f.	63			
20	r.s.	20·5	r.s.	2295·5	v.f.	59·5	s.		
18		18		86·5	v.f.	59			
		05	f.	82·5					
01	f.	01	f.	77·5	r.s.				
		2298	f.						
2295·5	f.	95·5	f.						
86	r.s.	87	r.s.						
82		82·5							
79	s.	78							
77		76							
31 bands		54 bands		60 bands		72 bands		75 bands	

(continued).

15·5 mm. λ.	9 mm. λ.	5 mm. λ.	4 mm. λ.
2356·5 r.s.			
54 v.f.		2355 v.f.	
49·5		52	
45·5 s.			
44			
2259·5 f.			
88 bands	52 bands	38 bands	30 bands

TABLE VII.—A Comparison of the Intensity of the Absorption Bands in the Vapour-Spectrum of Benzene (i.) at 100° C. and Different Pressures, and (ii.) at Temperatures below its Boiling-point, and Constant Pressure.

Strong bands and groups are indicated by one line, very strong by two lines, on the margin of the Columns I. and II.

Abbreviations:—f., feeble; s., strong; v.s., very strong; n., narrow; b., broad; v.f., very feeble; n.s., narrow strong.

I. λ.	II. λ.	I. λ.	II. λ.	I. λ.	II. λ.
	2757 f.	2587 } f.	2587·5 f.n.	2437 f.	2437 f.
	56 f.	} A pair	86 f.n.	33 f.	33·5 f.
	54 f.	85 f.	85 f.n.	30 f.	30 s.
2744 f.		83 f.	83 f.n.	28 f.	28 s.
40 f.	40 f.	81 f.	80 s.	24 f.	24 s.
36 f.	36	79 f.	78 f.n.		23 s.n.
32 f.		77	76·5 f.n.	20	21 s.
	15 s.	69	68 s.	18 f.	19·5 s.
09 f.	09 s.	67 f.	66 n.f.		15·5 v.s.
06 f.	03 s.	61 s.	60 f.	13 s.	13 s.
	2698 s.	57 s.	55 f.	09 f.	09 s.
2691 f.	91 s.	54 f.	54 s.		07 v.f.
89 f.	87 s.	51 s.	50 s.	00 s.	00 s.
80	79 v.s.	46 s.	46 s.	2394 f.	2394 f.
75	75 s.	44 n.f.	43 s.	86 f.	86 f.
69 s.	68 s.		40 s.	84 f.	83 f.
66 f.	66 f.n.	39 s.	38 s.	79 f.	77 f.
64 f.	64 f.n.	34 s.	35 s.	75 f.	75 s.
	62	29 s.	29 s.	72 f.	72 s.
60 s.	59 v.s.	26 s.	27 s.	68 f.	68 s.
58 f.	58 f.n.	22 s.			62·5 s.
54 f.	55 f.n.	21 f.	21 f.	61 f.	62 f.
50 f.	52	19 f.	19 f.	58 f.	58 f.
47 f.	48 f.n.	12 s.	12 f.	52 f.	52 v.f.
44 f.	44·5 f.	09 f.	09 f.	49 v.f.	49 v.f.
36 f.		05 f.	06 s.	43 f.	44 s.
34 n.	34 s.	01 f.	02 f.	30 f.	33·5 f.
33 s.		2499 s.	2498 s.	24 f.	24 s.
31 f.	32 s.	96 s.	96 f.	20 n.s.	18 s.
28 f.	28·5 f.	94 s.	92 v.f.	15 f.	
25 s.	26 s.	91 f.	90 f.	07 f.	05 f.
	24 f.	87 s.	87 v.f.		01 f.
21 f.	21 f.	86 n.f.	85 f.	2294 f.	2295 v.f.
19 s.	19 n.s.	81 s.	81 f.		82 s.
17 s.	17 s.	79 f.	79 f.	77 f.	77 s.
13 s.	13 v.s.	77 s.	76 f.	69 f.	
	11 s.	69 s.	69 f.	67 f.	63 s.
08 s.	08 v.s.	69 n.	68 s.	59 f.	59·5 f.
06 f.	05 v.s.	64 s.	64 s.	26 n.f.	
02 s.	02 v.s.	54 s.	54 s.		
2597 s.	2598 v.s.	52 f.	52 f.		
91 s.	92 v.s.	47 f.	48 f.		
89 f.	88 s.	39 f.b.	39 s.		

Observations.—From Table VII. it is at once seen that the absorption bands at 100° C. are almost identical with those at lower temperatures. At 100° C., however, the series of bands in the region near λ 2700 develops strongly, and the bands show a peculiar sharpness and definition; this series at lower temperatures is very ill defined, and the bands themselves appear feeble. There are many bands which appear faint in Column I. which are strong in Column II., and *vice versâ*; this change is not restricted to any one particular region of the spectrum, but extends throughout. As a rule, however, the strongest bands in the one column are the strongest in the other.

It has already been noted in the record of the spectrum of benzene vapour at temperatures below its boiling-point, that bands sometimes appear so close together that a separate measurement of each is impossible; at 100° C., on the other hand, these pairs are frequently so split up that each band is easily measurable, as, for instance, λ 2587, Column I., is a close but feeble pair; in Column II. it becomes λ 2587·5 and 2586, both being feeble and narrow.

Table VIII.—Absorption Bands in the Spectrum of Toluene Vapour at Different Temperatures and Constant Pressure of 751 mm.

Abbreviations:—s., strong; f., feeble or faint; n., narrow; v.s., very strong; b., broad; v.b., very broad.

Corresponding groups of bands are indicated on the different toluene spectra by the same Greek letters.

	10° C. λ.	30° C. λ.	40° C. λ.	50° C. λ.	60° C. λ.	70° C. λ.	80° C. λ.	90° C. λ.	100° C. λ.
	2689 f.	2689 f.		2690 f.			2690 f.	2695 f.	2695 f.
				87 f.	2689 f.	2688 f.	88 f.	90 f.	90
	82	82 f.	2682	83 s.	82 s.	82 f.	84 f.	85 f.	88
	79 } f.	79 } f.	75	78 } s.	78 } s.	77 } s.	78 } s.	82 s.	84 } s.
α	75 }	74 }	72 }	75 }	73 }	75 }	75 }	77 } s.	82 }
	73 } s.	72 } s.		72 } s.	72 } s.	72 } v.s.	72 } s.	74 }	78 } s.
	70 }	70 }	70 }	70 }	70 }	70 }	70 }	71 } v.s.	74 }
		51 } v.f.	51 } f.	54 } f.				69 }	72 } s.
							51 f.b.		70 }
		43 }	42 }	42 }			45 f.b.	51 } v.f.	51 } v.f.
								42 }	42 }
	41 } s.	41 } s.					41 } s.		
			40 } s.	40 } s.	40 } s.	40 } s.	40 }	40 } s.	41 } s.
β	38 }	38 }	37 }	37 }	37 }	37 }	37 } s.	36 }	36 }
	36 } s.	35 } s.						35 } s.	35 } s.
	34 }	33 }					33 }	33 }	33 }
		31 f.					31 f.		
				11 f.				10 f.	

TABLE VIII. (continued).

	10° C. λ.	30° C. λ.	40° C. λ.	50° C. λ.	60° C. λ.	70° C. λ.	80° C. λ.	90° C. λ.	100° C. λ.
	2610	2608	2608	2608	2608	2609	2608	2608	2607
	07 } s.	06 } s.	06 } s.	06 } s.	06 } s.	06 } s.	} s.	} s.	
γ	06	05	05	05	05 s.	05 s.	05	05	} f.
	05 } n.	04 } s.	04 } s.	04 } s.			05	05	03
		02					04 } s.	03 } s.	
		2599 } f.			00				
	2596	96							
	94 } s.	94 } f.			} s.				
δ	91	91	91	91	2591				
	} s.	} s.	} s.	} s.	90				
	89	89	89	89	88 } s.				
	72 f.	71 f.	72	71 f.	71 f.	71 f.	71 f.	70 f.	71 f.
	69 f.	68 f.	68 } f.	68 f.	68 f.	69 f.	68 f.	68 f.	68 f.
	54	54 f.	54 f.	53 f.	53 f.		53·5 f.	53 f.	53 f.
	44	43		46	45	46	46	43	
	42 } s.	41 } s.	41 s.	41 } s.	41 } s.	41 } s.	41 } s.	41 } f.	
η	33	33	33	34	33	33	33	33	34
	32 } s.	30 } s.	30 } s.	30 } s.	30 } s.	30 } s.	30 } s.	29 } s.	30 } f.
					27 f.				
θ	2474	2474	2474	2474	2473	2474	2774	2474	2473·5
	71 } s.	71 } s.	71 } s.	71 } s.	71 } s.	71 } s.	71 } s.	71 } s.	71 } s.
		20 f.	20 f.	20 f.	23	24	24	24	24
					17 } f.	17 } f.	18 } f.	13 } v.f.	
					11 f.		11		
								09 f.	
					03		} b.v.f.		
					2397 } v.f.	01			
						} v.f.		03	
						2391	2391		} v.b.
					81	82	83		
					75 } v.f.	75·5 } v.f.	75 } v.f.	} v.b.f.	
					59 f.	59			
					2355		2353 f.		
								2342	
						2349 v.f.			
									2328
	16 bands	20 bands	14 bands	18 bands	22 bands	17 bands	22 bands	21 bands	16 bands

TABLE IX.—The Absorption Spectrum of Toluene Vapour at Different Pressures and Constant Temperature of 11° C.

Abbreviations :—s., strong ; f., feeble or faint ; v.f., very feeble ; b., broad.

Corresponding groups of bands are indicated on the different toluene spectra by the same Greek letters.

	763 mm. λ.	563 mm. λ.	371 mm. λ.	174 mm. λ.	43 mm. λ.
	2695 f.				
	88 f.		2688 f.		
	84 f.		84 } s.		
		2682 f.	82		
				2681 f.	2681 f.
α	75 f.	75 f.	76 } s.		75 } f.
			73	73 f.	73
	72 } s.	72 } s.	72 } v.s.	72 } s.	72 } f.
	70	70	70	69	69
	51 f.				
	46 f.		46 } f.		
β	41 } s.	39 } s.	43		
	36	36	39 } s.	39 } s.	39 } s.
	35 } s.	35 } s.	37	36	36
	33	33	35 } s.	34 } s.	34 } s.
		30 } v.f.b.	30	32	31
			29 } f.		
	22 } f.	22	22		
	19	21 } f.	20 } f.		20 } f.
		18	17	19 } f.	17
			16 f.	16	08 f.
γ	08 } f.	07 } s.	07 } s.	07 } f.	07 } f.
	06	05	05		05
	05 } f.	05 } s.	04 } s.		
	03	02	02	02	02 f.
δ	2594 } f.	2595 } f.	2595 } f.	2594 } f.	
	91	90	91		2591 f.
	90 } f.	89 } f.	90 } f.	90	
	87	87		89 } f.	89 } f.
			87	87	87
			76 } f.	70 f.	70 f.
			68	67 f.	67 f.
				59 } f.	
		54 } f.		54	
η	41 } f.	52	52 } f.b.	52 f.	52 f.
	38	43 } f.			
	33 } s.	38			
	30	30	31	30 f.	
θ	2471 f.	2471 s.	2471 f.	2470 f.	2470 f.
	19 f.	19 f.			
	18 bands	16 bands	17 bands	15 bands	15 bands

TABLE X.—Absorption Bands in the Spectrum of Ethylbenzene Vapour at Different Temperatures and Constant Pressure.

Abbreviations:—s., strong; b., broad; f., feeble or faint; v.s., very strong.

(Photographic Plate 5*a*, 31.5.06.)

Corresponding groups of bands are indicated in the different spectra by the same Greek letters.

16°·5 C. λ.			40° C. λ.			70° C. λ.			100° C. λ.		
α	2673 72			2681 78	f.		2681 77	b.		2716 13	s.
	70 67		α	75 67	s.b.	α	73 67	s.		10 06	s.
	41 39	s.		57 43	f.b.		52 45	b.			
β	37 35	s.	β	40 39	f.	β	42 34	f.			
New ε	33 32	s.		36	f.	ε	33	f.			
	31 28	s.	ε	30	f.		29	f.			
	09 07	f.		29 25							
γ	06 05	s.	γ	06	f.						
New ζ	03 01	s.	ζ	02	f.						
	2597 94	v.s.	δ	2596	f.						
δ	93 86	b.		72 64	b.						
New ι	84 82			62 59	f.						
	71 63	f.b.		56 51	f.						
η	45 43	s.	η	46 43	f.						
	40 38	s.		40	f.						
	35 32	s.		35	f.						
θ	2476 73	s.		2480	f.						
	20 18		θ	76 73							
				22	f.						
				20 19			2420	f.			
	2379	n.		2379·5	n.		2379	n.			
	19 bands			18 bands			8 bands			2 bands	

NOTE.—In the above spectra there is an intense general absorption between λλ 2678 and 2329; the powerful line, Cd 18, λ 2573 being quite blotted out. The absorption increases in intensity with rise in temperature, until at 100° C. all but two bands have disappeared.

A distinguishing feature in this spectrum is the appearance of four new bands: λλ 2632–33 s., 2628–31 s., 2601–03 s., and 2582–84. They do not occur in the spectra of either benzene or toluene.

TABLE XI.—Absorption Bands in the Spectrum of Ethylbenzene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—s., strong ; b., broad ; f., feeble or faint ; v.s., very strong.

(Photographic Plate 5*b*, 5.9.06.)

	20° C. λ.			36° C. λ.			52° C. λ.		71° C. λ.		100° C. λ.
	2671	s.		2671	b.s.		2689	f.	2421	f.	
	69		α	63			81		15·5		
α	69	s.		40	f.	α	78	s.b.	12	f.	Complete absorption of all rays between λλ 2716 and 2331. Cd 18 not visible.
	67		β	36			63		02		
	66	n.		35	f.		58	b.v.f.	2366	v.f.	
	40	f.		32			23				
β	36			31	s.		18	v.f.			
	35	s.	New ε	25			17				
	33			20	f.		2365	v.f.	Cd 18 very faintly seen through the general absorption extending from λλ 2654 to 2475.		
New ε	31	s.b.		18							
	14			16	f.b.						
	05	s.	γ	02			General absorption very strong on either side of Cd 18, this line being very faintly visible.				
γ	03			01	f.						
	02	s.		2598							
	2599		δ	94	s.						
	97	n.f.		91							
δ	95	s.		53							
	91			47							
	88	v.f.		45	s.						
New ι	84		η	40							
	82	v.f.		38	s.						
	80			35·5							
	54	f.		31	s.						
	49			29							
	43	s.	θ	2472							
	41			70							
η	38	s.		18	s.						
	35·5			16							
	32	s.		2363	v.f.						
	30										
θ	2473	s.									
	71										
	18	f.									
	17										
	2365	v.f.									
	17 bands			15 bands			5 bands		3 bands		

The bands of the ε group are difficult to measure because they become merged into one broad band by the over-lapping general absorption at temperatures above 40° C. See Table X.

TABLE XII.—Absorption Bands in the Spectrum of Orthoxylene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—s., strong ; f., feeble or faint ; b., broad.

(Photographic Plate 6, 1.6.06.)

20° C. λ.	45° C. λ.	Observations on the spectra at higher temperatures.
2696 94 s.	2710 2695 b.s.	At 72° C. All rays were transmitted as far as λ 2738, and absorbed from λ 2738 to 2497. From λ 2497 they were again transmitted to 2243, but very feebly to λ 2332.
91 90 s.	95 94 s.	At 100° C. Rays transmitted to λ 2738. An intense absorption continued from λ 2738 to 2421. Rays were transmitted from λ 2421 to 2265.
89 84 s.	91 89 s.	At 121° C. Rays were transmitted to λ 2800, and intensely absorbed from λ 2749 to 2332. They were transmitted again from λ 2332 to 2269.
60 58 s.	87 83 s.	
57 52 s.	78 77 f.	
50 47 s.	71 66 f.	
42 39 f.	63 60	
36 f.	59 56	
19 f.	52 50	
12 09 s.	47 45	
08 05 s.	44 42	
02 01 s.	41 39	
2597 94 f.	36 33	
91 86 f.	30	
72	19 f.	
71 69 f.	16 f.	
63 f.	01 f.	
61 f.	2594 f.	
52	84 f.	
49 46	70	
45 42	59 f.	
40 38		
26		
23 bands	21 bands	

TABLE XIII.—Absorption Bands in the Spectrum of Metaxylene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—s., strong ; f., feeble ; b., broad ; v.b., very broad ; n., narrow.

(Photographic Plate 7, 30.3.06.)

11° C. λ.		40° C. λ.				70° C. λ.		100° C. λ.	
2713 08	b.	2673 71		2481		2689		2732 26	
05 2698	b.	70 68		78		79 65	v.b.	19	f.
94 89	f.	67 64		74 71	s.	60 28	v.b.	16 10	f.
44 42		51 45		32		2420 18		2368 64	
36		42 39		29		2366 64		26	
34 28		36 34		22	n.	26			
09	n.	32		20		Between λλ 2612 and 2504 there is a strong absorption band.		Between λλ 2652 and 2429 there is intense absorption. The rays from λ 2429 to 2241 are transmitted.	
06	n.	30 28		19 17	s.				
03 01		25		2379					
2597 95	s.	22		77					
44 43	n.	19		67 64					
38	f.	18 16							
34 32	s.	13 10							
06	n.	08 04							
01	n.	02 2599							
2498 94	f.	97 94	s.						
94	n.	90	f.						
90	n.	83 78							
84	n.	57							
82		54 52							
79		51 49							
75 73	s.	46 41							
71		40 37							
22	n.	35 30	s.						
19 18		27							
2377 75		04							
		01	n.						
		2491	n.						
		89	n.						
		83 82							
26 bands				41 bands		7 bands		6 bands	

It is a distinguishing feature of the bands in the metaxylene vapour spectrum that all more refrangible than λ 2600 are narrower and better defined than those in paraxylene, and again the bands in the latter are better defined and less diffuse, although broad, than those in the spectrum of orthoxylene.

TABLE XIV.—Absorption Bands in the Spectrum of Paraxylene Vapour at Different Temperatures and Constant Pressure.

Abbreviations:—s., strong; f., feeble or faint; b., broad; n., narrow; s.b., sharp, broad; s.n., sharp, narrow; f.n., faint, narrow; f.b., feeble, broad.

10° C. λ.	40° C. λ.	70° C. λ.	100° C. λ.
2747 39 } b.	2747 39 } b.	2791 84 } b.	2802 f.n.
38 32 } b.	38 32 } b.	77 n.	00 2795 } f.b.
30 26 } b.	30 26 } b.	73 68 } b.	94 85 } b.
19 14 } f.b.	22 19 } f.	66 n.	83 78 } f.b.
00 f.	16 12 } b.	63 50 } b.	77 69 }
2688	09 06 }		66 n.
78 70 } s.b.	02 2698 } b.	There is intense absorption from λ 2762 to 2416. The rays from λ 2416 to 2265 are transmitted. Hence the above is an intense and very broad absorption band.	65 52 }
68 s.n.	94 85 } b.		
65 54 } b.	83 n.		There is an intense absorption band from λ 2790 to 2416. The rays from λ 2416 to 2288 are transmitted.
52 47 } b.	81 n.		
45 44 }	78 69 } b.		
42 41 }	68 n.		
34	65 55 } b.		
33 30 }	52 47 } b.		
24 f.	42 40 }		
22 19 }	35 f.		
18 15 }	31 f.		
12 n.	25 n.		
06 02 } f.	23 19 } b.		
2599 n.	19 14 } b.		
97 88 } b.	12 11 }		
87 n.	2597 87 } b.		
66 62 } f.	85 n.		
60 n.	62 f.		
54 52 } f.	60 f.		
41 37 } b.			
36 34 } f.			
33 32 } f.			
16 07 } f.			
00			
30 bands	25 bands	6 bands	8 bands

TABLE XV.—Absorption Bands in the Spectrum of Cymene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—f., feeble ; b., broad.

17°·5 C. λ.	40° C. λ.	70° C. λ.	100° C. λ.
Weak bands not easily measured	2719 13 } f.	2720 15 } b.	2726 13 }
	2676 72 } f.	14 08 } b.	12 07 }
	69 61 } f.	2677 73 } b.	2676 72 }
	58 42 } f.	69 61 } b.	68 60 }
	38 32 } f.	60 53 } b.	58 52 }
	28 21 } f.	49 42 } b.	38 34 }
	2592 81 } f.	38 34 } b.	32 24 }
		28 19 } b.	2599 93 }
		2591 87 } b.	91 84 }
	7 bands	9 bands	9 bands

All rays beyond λ 2580 are completely absorbed.

TABLE XVI.—Absorption Bands in the Spectrum of Mesitylene Vapour at Different Temperatures and Constant Pressure.

Abbreviations : — f., feeble ; v.b., very broad.

18°·5 C. λ.	45° C. λ.	72° C. λ.	100° C. λ.	120° C. λ.	140° C. λ.
2717 12 } f.	2717 12 } f.	2717 12 } f.	2737 07 } f.v.b.	Very feeble throughout.	All rays absorbed beyond λ 2749
09 05 } f.	09 06 } f.	12 06 } f.			

All rays beyond λ 2705 are completely absorbed.

TABLE XVII.—Similar Groups of Absorption Bands which occur in the Vapour Spectra of Benzene, Toluene, Ethylbenzene, and the three Isomeric Xylenes.

Benzene and Toluene are compared at ordinary temperatures, and also at 30° C. below their respective boiling-points, at atmospheric pressures.

Abbreviations:—s., strong; f., feeble; n., narrow; b., broad; v.s., very strong.

	Benzene. 12°·7 C. λ.	Toluene. 10° C. λ.	Benzene. 50° C. λ.	Toluene. 80° C. λ.	Ethyl-benzene. 20° C. λ.	*o*-Xylene. 20° C. λ.	*m*-Xylene. 11° C. λ.	*p*-Xylene. 10° C. λ.
			2690 } f.	2690 f.				
			88 }	88 f.				2688
			80	84 f.				
α	2678 } b.	2679 } f.	78 } f.	78 } s.				78 } s.b.
	76 }	75 }	75 }	75 }				70 }
	72 } s.	73 } s.	72 } s.	72 } s.	2670 } s.			
	70 }	70 }	70 }	70 }	67 }			
				51 f.b.				
				45 f.b.			2644 }	
		41 } s.	40 } f.	41 } s.	41 } s.	2642 } f.	42 }	42 }
β	39 f.	38 }	37 }	40 }	39 }	39 }		41 }
	36 f.	36 } s.	36 } f.	37 } s.	37 } s.	36 f.		
	34 f.	34 }	34 }	33 }	35 }			33 }
	31 f.		31 s.	31 f.				30 }
γ	12 } s.	10 } s.	11 } s.	08 } s.	09 } s.	12 } s.	09 n.	
	08 }	07 }	08 }	05 }	07 }	09 }		
	06	06 } s.	07 } s.	05 } s.	06 } s.	08 } s.		
	05 } s.	05 }	02 }	04 }	05 }	05 }	06 n.	06 } f.
	03 }							02 }
δ			00 } s.	2595 } s.	2597 } v.s.	2597 } f.	2597 } s.	2597 } b.
	2597 } s.	2596 } s.	2597 }	93 }	94 }	94 }	95 }	
	95 }	94 }						
	90 s.	91 } s.	97 } s.	90 } s.	93 } b.	91 } f.		
		89 }	91 }	88 }	86 }	86 }		88 }
	72 f.	72 f.	69 f.	71 f.		71 } f.		
			67 f.	68 f.		69 }		
			51 f.	53·5 f.				
η	43 n.							
	42 } s.	44 } s.		46 } s.	45 } s.	45 }	44 } n.	
	40 }	42 }		41 }	43 }	42 }	43 }	
					40 } s.			
					38 }			
	33 } s.b.	33 } s.		33 } s.	35 } s.		34 } s.	33 } f
	29 }	32 }	27 s.	30 }	32 }		32 }	32 }
θ	2474 } s.b.	2474 } s.		2474 } s.	2476 } s.			
	71 }	72 }		71 }	73 }			
				24 } f.				
				18 }				
			09 f.	11 } b.f.				
			95 f.					
				2391 }				
				83 } f.				
				75 }				
			49 f.	53 f.				

TABLE XVIII.—Table of Wave-length Measurements of the Heads of Strong Bands which appear to be Common to Benzene and its Homologues.

Abbreviations :—f., feeble ; n., narrow.

Benzene.	Toluene.	Ethylbenzene.	*o*-Xylene.	*m*-Xylene.	*p*-Xylene.	Cymene.	Mesitylene.
*2670	2670	2667	—	2668	2670	2672	—
2639	2638	2639	2639	2642	2641	2642	—
2634 f.	2634	2635	2636 f.	2634	2630	2634	—
*2608	2607	2607	2609	2609 n.	2611	—	—
*2603	2605	2605	2605	2606 n.	2602 f.	—	—
*2595	2594	2594	2594	2595	2597 ⎫	2593	—
*2590	2589	2586	2586	2590 f.	2588 ⎭	2587	—
*2540	2542	2543	2542	2543	—	—	—
*2529	2532	2532	—	2532	—	—	—
*2471	2472	2473	—	2473	—	—	—

* The bands marked thus are those which appear strongly throughout this group of hydrocarbons.

On the Relation of the Absorption Bands in the Spectrum of Benzene Vapour at Atmospheric Pressures and Temperatures to the Bands Observed in Solutions of Benzene in Alcohol.

PAUER compared the groups of bands in the absorption spectrum of benzene with the bands observed in the liquid itself and in solution in alcohol. The total number of bands observed in the vapour was 29, in a column 10 cm. long, containing atmospheric air charged with benzene vapour at a temperature of 20° C. These he divided into four groups, with three additional bands commencing as it were a fifth group. He assigns five bands to the liquid and to the solution respectively. He describes the spectrum of the vapour as being composed of fine lines. That they have this appearance is probably due partly to the low temperature and small quantity of the benzene examined, and partly to the small dispersion of his instrument, which was fitted with one Cornu's quartz prism of 60° and quartz lenses of short focus, achromatised with fluor spar. The angle of inclination of the photographic plate to the normal of the lens would thus be not much less than 90°, whereas with uncorrected lenses it would be approximately 22°.

The greater the length of focus of the lenses, if of plain quartz, the greater is the separation of the lines; thus, if the focus for the line D, λ 5893, be about 900 mm., that for Cd 26, λ 2144, will be 776 mm., making a difference of about 5 inches, and on photographs taken with a dispersion of only one quartz prism and such lenses the linear distance measured between Cd 17, λ 2748, and Cd 26, λ 2144, is 87 mm., the last line showing a fine reversal. This affords evidence of accurate focussing and perfect definition.

With a quartz train consisting of two half prisms of 30° of opposite rotation to a single prism of 60°, the lenses being of 325 mm. focus, the linear distance between the same lines measured on a photograph is about 55 mm. (See 'Chem. Soc. Trans.,' 1898, vol. 73, p. 695.)

The absorption spectra of a series of solutions of benzene were photographed by HARTLEY and DOBBIE with the quartz train of three prisms, and it was observed that the bands were sharpest where the rays are of shorter wave-length, and are gradually weakened in the opposite direction as if they were composed of groups of lines or very narrow bands, closer together and stronger on the side of the least refrangible rays. Both FRIEDERICHS and GREBE have compared the positions of the heads of the bands in these spectra with respect to the heads of the groups in the vapour spectra of the same substance as measured by them. Shortly described, the differences between the spectra of the solution and the vapour are such that the former are very broad and few in number, the latter multitudinous, very narrow, and arranged in groups. The corresponding bands and groups in the spectra of the two different states differ in the bands of the solution being shifted by a definite number of wave-length differences towards the less refrangible rays, both the bands and groups of bands being degraded in the same direction. This is shown on reference to fig. 7, where the spectra of exactly the same quantity of benzene, in the state of vapour and of solution, are photographed on the same plate, at the same time, and with the same exposure. Here it may be remarked that the displacement is not at all evident from PAUER's measurements, which are here quoted.

Heads of bands . .	I.	II.	III.	IV.	V.
	λ.	λ.	λ.	λ.	λ.
Solution	2590	2535	2480	2420	2360
Vapour.	2592	2528	2467	2412	2362

Of the more recent series of numbers taken for comparison, the measurements made by GREBE exhibit a greater regularity in their differences than those quoted by FRIEDERICHS. It will be convenient to name the spectra of the vapour *vapour spectra*, and those of solutions *solution spectra*. As neither the quantity of substance in the state of vapour, nor the barometric pressure at the time, were taken into account by PAUER, FRIEDERICHS, and GREBE, and as the two latter experimenters do not mention the temperature at which the benzene was vaporised, it is difficult to make a strict comparison with their measurements; but it will be seen that the regularity in the differences is more striking if the benzene *vapour spectrum* at 12°·7 C. and barometer 759·5 mm. is compared with the alcoholic solution containing very nearly the same quantity of benzene, since the conditions under which the former were photographed correspond more closely with those under which the solutions were examined. The following tabulated statement will render this evident :—

Heads of bands	I.	II.	III.	IV.	V.	VI.
	λ.	λ.	λ.	λ.	λ.	λ.
Solution spectrum	2681	2599	2541	2483	2429	2376
Vapour spectra :—						
(1) Greebe	2665	2587	2526	2463	2412	2360
Differences	16	12	15	20	17	16
(2) At 12°·7 C. and 759·5 mm. bar.	2670	2589	2528	2469	2416	2365
Differences	11	10	13	14	13	11
(3) At 11°·5 C. and 778 mm. bar.	2669	2591	2527	2470	2413	—
Differences	12	8	14	13	16	—

The measurements taken from *vapour spectrum* (3), at 11°·5 C. and 778 mm. bar., show the absorption to have so greatly increased that Band VI. has entirely disappeared.

The difference between the *solution spectrum* and the *vapour spectrum* at 12°·7 C. and 759·5 mm. bar. is that the former is shifted from 10 to 14 Ångström Units in the direction of the less refrangible rays.

On the photograph fig. 4, it will be seen that both the *solution bands* and the groups of *vapour bands* fade away in the direction of the visible rays. Owing to the weakness of the continuous rays beyond λ 2329, which is partly caused by the general absorption exerted by the benzene thereabouts, it is desirable that those bands which clearly appear on the original photograph fig. 4 should be recorded because the printing process does not reproduce them. There are also bands which become too indistinct under the magnifying power used to admit of their being accurately measured with the micrometer, although quite visible under ordinary inspection.

Vapour Bands.—One band is seen at λ 2200, and several near λλ 2194 and 2234. One band at least is visible between λλ 2265 and 2238. Two bands about λ 2300, one of these is at 2279. One band is seen at λ 2326, and another between λλ 2321 and 2318. There are several very definite bands about λ 2700. These are all in addition to those of which measurements have been already recorded.

Solution Bands.—The general absorption caused by the benzene solution is so intense as to completely obliterate the strong cadmium lines λλ 2194, 2144, and 2114, and also the continuous rays which otherwise are seen to occupy the spaces between them. Three bands occur with heads at λλ 2600, 2616·5, and 2642, and another, commencing at λ 2682, extends towards the less refrangible rays.

Between the vapour spectra (2) and (3) there is an important difference due to the lowering of the temperature by 1°·2 C., and increasing the pressure by 23·5 mm. The quantity of benzene was practically the same in both cases: in (2) the weight found was 0·0179 grm., and in (3) that calculated from the vapour pressure was 0·0175 grm. The difference is seen in (3), where the increased general absorption cuts off Band VI. entirely. It also widens the absorption bands, so that the heads are measurable at a point from 1 to 3 Ångström Units extended towards the rays of shorter wave-lengths.

A *solution band* is thus seen to be the aggregate effect of the absorption of rays caused by a group of *vapour bands*, which is modified by the greater density, and consequently greater dispersion, of the liquid medium in which the substance is dissolved, and it is shifted towards the red in accordance with KUNDT's rule (A. KUNDT, 'Pogg. Ann.,' Jubelband, 1874, p. 620). The slightly different positions of the *four vapour spectra* (see map, p. 484), their similarity in constitution, and the manner in which they overlap, afford an explanation of the reason for the spectrum of benzene being composed of six principal groups of *vapour bands* and six corresponding *solution bands*. The constitution and properties of the *vapour spectra* account also for four of the *solution bands* being similarly constituted, and of greater width and intensity than the others, with approximately the same persistency or coefficient of extinction; they also account for the isolated narrow bands at each end of the spectrum. It is evident, on examining the map (on p. 484) and comparing it with the photographs (figs. 1 and 4), that where the four vapour spectra overlap to the greatest extent, the four most regularly constituted and intense groups of bands are to be found, and the four most intense *solution bands* naturally occur. At either end, where the overlapping is less complete or does not occur, the first and sixth *solution bands* are situated, and likewise the narrow and unimportant groups and isolated bands. Under certain conditions, such as diminished pressure or increased temperature, other feeble bands of the vapour appear distinctly at either end of the spectrum, and with reduction of pressure they become strong bands at the less refrangible end. A further noticeable feature in each of the four *vapour spectra* is that the bands are generally grouped together in threes and fours, also occasionally in fives, and as this affects the constitution of the *solution bands*, and particularly their width, it possibly may account for their number being six.

The Homologues of Benzene.

It has been shown that a displacement of the general absorption towards the less refrangible rays in *solution spectra* is caused when the molecule is loaded by the replacement of one or more H atoms in benzene by elements of greater atomic weight, or by radicals or complex groupings such as Cl, Br, CH_3, C_2H_5, or $CH{\cdot}CH_3{\cdot}CH_3$, the displacement being the greater the heavier the load. As regards the selective absorption, there is a complete divergence from the spectrum of benzene, inasmuch as one broad band and two or more narrow ones, or a single broad band, takes the place of the several bands characteristic of this hydrocarbon. Isomeric hydrocarbons differ from one another, each having its own peculiar spectrum, even when the isomerism is due to the positions of the substituted hydrogens in the benzene ring. That which has been observed with respect to *solution spectra* has been ascertained by the foregoing experiments to apply to *vapour spectra*. This was recognised also by PAUER. It is more particularly evident in the *vapour spectra* of the three xylenes, in cymene, and in mesitylene, that several groups of narrow bands are merged into one broad band, the measurements of which, as regards breadth, intensity, and position in the spectrum, are different for each substance; at the same time the general absorption is shifted towards the less refrangible rays and is sometimes greatly increased. This suggests not only a lowering of the kinetic energy of the molecules, but some irregularity in their motion which gives rise to an increased number of shocks or encounters (see Tables XII., XIII., XIV., and XVI.).

After a careful examination of the tables of wave-length of *vapour bands* and comparing them with the photographs, it does not appear to be evident that the greater molecular weight of a benzene homologue shifts all the bands towards the red, though it is apparent that certain of the bands are so shifted; it is also clear that certain groups of bands are common to benzene, toluene, ethylbenzene and *o*-xylene, and that these are the bands affected. But the weighting of the molecule, besides diminishing the number of the *vapour bands*, causes the general absorption to extend further towards the rays of longer wave-length. At constant pressure the effect of rise of temperature might be expected to cause an increased number of molecules to cross the path of the rays, which is the same in effect as increasing the quantity of substance, or lengthening the column of vapour; reduction of pressure would therefore be expected to have an opposite effect, by reducing their number and increasing the mean path of the molecules—the absorption bands, if caused by vibrations within the molecule, would as a consequence become more distinct. This is, in fact, what is actually seen in the least refrangible groups, between λλ 2750 and 2500, particularly when benzene vapour is maintained at 100° C. and the pressure is gradually reduced to 4 mm. (See fig. 2; for the wave-lengths also Table VI.) The quantity of benzene in the 79 c.c. is only 0·0011 grm. in weight, at 4 mm. pressure.

It has been experimentally shown that increase of mass, of density, and of temperature operate in the same manner upon the rays entering a column of benzene vapour: in the first place, the general absorption is increased by an extension towards the visible rays and it is also intensified; in the second place, the bands of absorption broaden, become diffuse, and coalesce. As the bands attributed to the internal vibrations of the parts of the molecule in different isomeric hydrocarbons become diffuse and coalesce, partaking of the character of the general absorption, and as this is not confined to one part of the spectrum, namely to the less refrangible or transmitted rays, but is a selective absorption, it cannot be due to simply a loading of the molecule; if it were, then it would be impossible to distinguish between the three isomeric xylenes, or to identify them by a simple inspection of their absorption spectra, or even to distinguish them from ethylbenzene.

It may be conceived to be due in part to an irregularity in the motions of the molecules, such as would arise from encounters between unsymmetrically shaped bodies; or if of symmetrical form, such as vortex rings or spheres, the rings or spheres being not throughout of uniform density; in other words, the distribution of mass within the molecule being different for each isomer.

The same effect upon the spectrum as that due to a want of uniformity in the distribution of the mass of the parts within the molecule could be brought about by periodic contractions and expansions occurring within it.

It is conceivable that it might be caused by a transference of a part of the intra-molecular energy to the kinetic energy of the molecule, the intra-molecular vibrations being actuated by the radiant energy of the spark.

A striking feature in all the benzene homologues examined is the existence in their spectra of certain bands which remain unaffected by temperature and pressure, and these bands are common to all the substances, whether they be isomeric substances or not. They are the bands which are subject to displacement when the molecules are weighted, and their displacement is uniform and measurable in Ångström Units.

It is necessary to refer to the constitution of the *solution spectrum* of benzene as photographed by Messrs. BALY and COLLIE, because they have ascribed to benzene exactly seven, and no more than seven, *solution bands* ('Chem. Soc. Trans.,' 1905, vol. 87, p. 1332).

The head of a band appears at wave-length 2656, and this they consider to be the second of the *solution bands*. Every *solution band* must have its origin in a group of *vapour bands*, or it may be derived from a single *vapour band*. A study of the vapour spectrum under varying conditions of temperature and pressure shows that the second *solution band*, which is narrow and of very feeble intensity at ordinary temperatures, is not represented by any corresponding band or group in the vapour spectrum at the same temperature and with the same quantity of substance which gives rise to six groups of bands.

At a temperature of 45° C. and barometer 759·5 mm. the vapour spectrum has two feeble narrow bands at wave-lengths 2636 and 2633. FRIEDERICHS and also GREBE measured a vapour band at λ 2633, which apparently corresponds to the solution band measured by BALY and COLLIE at 2656, but it is narrow and feeble, and there is no strong band or group near with which it might be confounded. The same *solution band* has been photographed (HARTLEY and DOBBIE, 'Chem. Soc. Trans.,' 1898, vol. 73, p. 695), but it was found to be too feeble to be measured, and also it was different in character from the six principal bands. Moreover, its position was so close to the first band at the least refrangible end that it might easily have been mistaken for an extension of it caused by dilution or by decreasing the quantity of substance.

A narrow and feeble *solution band* was measured at λ 2330, which Friederichs considered as corresponding to a *vapour band* measured by him at λ 2305. It has a considerable intensity, inasmuch as it withstands dilution to a far greater extent than the band under discussion ; it is the eighth band.

Furthermore, a ninth band has been photographed, which apparently corresponds to the ninth group of *vapour bands* measured by Friederichs (see p. 493).

That six, and not seven, bands have generally been referred to as the characteristic feature of the benzene *solution spectrum* arises from the fact that six bands appeared to be similarly constituted, that is to say, each of them was sharpest and strongest at the more refrangible side, and became gradually weaker and less well defined on the side towards the red, but in the seventh feeble band this constitution was not evident. The greatest importance has always been attached to the four strongest bands, because, as already intimated, they are of similar intensity and constitution, and occur at approximately regular intervals. Moreover, there are similar groups of four bands in the spectra of naphthalene and anthracene (' Trans. Chem. Soc.,' 1898, vol. 73, p. 695).

The following tabulated statement of the numerical values in wave-lengths of the intervals (or transmitted rays) between each two successive absorption bands—that is to say, the space between the tail of the first and the head of the second band, and so on, with the differences between the more refrangible edges of successive bands—is of a particular interest in this connection :—

Solution Bands of Benzene.

(Hartley and Dobbie) Band.	Intervals, or transmitted rays, separating successive bands measured in Ångström Units, with the wave-length measurements of the width of the bands.	Differences in wave-lengths between the more refrangible edges of successive bands.
I.	2709 to 2681	82
	Interval 63	
II.	2618 to 2599	58
	" 45	
III.	2554 to 2541	56
	" 44	
IV.	2497 to 2485	56
	" 48	
V.	2437 to 2429	53
	" 50	
VI.	2379 to 2376	46
	" 32	
VII.	2344 to 2330	

The four principal solution bands are indicated by the bracket in the last column, showing regular differences in wave-lengths varying between 58 and 53 Ångström Units between the more refrangible edges of successive bands.

Comparison of the Wave-lengths of the Heads of Bands in Solution and Vapour Spectra yielded by the same Quantity of Benzene (see fig. 7, Plate 32).

Heads of bands.			Differences. Ångström Units.	Number of band.	Differences in wave-lengths between the heads of successive bands. Ångström Units.	
	Solution. λ	Vapour. λ.			Solution.	Vapour.
	2682	2670	12	I.		
					40	40
(1)	2657 2642	2630	12	II.		
					25·5	
(2)	2630 2616·5			III.		40
					16·5	
	2614 2600	2590	10	IV.		
					61	67
	2539	2523	16	V.		
					59	57
	2480	2466	14	VI.		
					50·5	51
	2426·5	2411	15·5	VII.		
	2376	2360	16	VIII.		
						34
		2326		IX.		
						47
		2279		X.		

Note.—(1) A feeble band, the width of which is measured; it appears to correspond with a feeble band in the vapour, λ 2630. (2) These two bands appear to be the result of the splitting of a broad band, the head of which is at λ 2600. It corresponds to the vapour band at λ 2590.

It will be remarked that in the first series of bands taken from solution spectra there are only seven, in the second there are eight, and in the vapour spectrum there are nine bands. Here again it will be seen, also, that the differences between corresponding bands in *solution* and *vapour* spectra respectively, as was shown on p. 519, amount to from 10 to 16 Ångström Units, which represent the shift towards the visible spectrum of different bands measured in solutions.

Summary and Conclusions.

The variations in the *vapour spectra* at different temperatures and pressures may be explained by the fact that there are two kinds of absorption which are sharply defined and may be differentiated; these are distinguished by the terms general and selective absorption. First, by rise of temperature, the general absorption is broadened and extended towards the less refrangible rays, the effect of which is to cause not only the narrow absorption bands but also the emission spectrum of metallic lines and diffused rays to become obscured, while the feeble narrow bands become strong and increase in number in that part of the spectrum which is unaffected by the general absorption. By reduction of pressure, temperature being constant, the general absorption is decreased, so that, consequent upon a diminution in the quantity of substance under observation in the tube, the narrow absorption bands become more numerous, but neither by rise of temperature nor reduction of pressure is the position of these bands altered. Secondly, the selective absorption is manifest in all the narrow individual bands and groups of bands, such as those that have just been referred to as unaltered in position by variations in temperature and pressure. The former, or general, absorption appears to be due to the translatory kinetic energy of the molecules. The selective absorption is to be explained by the vibrations of the atoms or atom-complexes within the molecules, so that they are not affected in the same manner as the translatory molecular movements by rise of temperature; they are not subject to displacement. When a larger number of molecules passes the slit, a greater number of the intra-molecular vibrations is brought into the field, and therefore feeble bands become intensified. Also bands not discernible at ordinary temperatures become apparent, and more intense as the temperature of the vapour rises. Moreover, by reduction of pressure and consequent greater duration of undisturbed motion of the molecules, the bands attributed to the intra-molecular vibrations become sharp and distinct.

The selective absorption is best studied by raising the general absorption to a maximum (at 100° C.) and studying the spectra as modified subsequently by reduction of pressure. By proceeding in this manner the changes in the spectra due to the general absorption may be eliminated (see figs. 3 and 4, Plate 33).

The Homologues of Benzene and Isomeric Substances.

In toluene and ethylbenzene spectra it is shown (1) that there are bands and groups of bands apparently having the same origin as those in benzene, and they are similarly constituted, but by the weighting of the molecule they are shifted into rays of less refrangibility, that is to say, with reduced oscillation frequencies; (2) there are bands which do not suffer displacement, but appear to be common to benzene and its homologues; (3) by increase of temperature and reduction of pressure the homologues of benzene suffer less change in the constitution of their spectra than benzene itself. Thus the bands and groups of bands are not affected to the same extent, neither is their number so largely increased or their intensity so augmented.

The principal changes in the spectra of *ortho-* and *para-*xylene, occasioned by rise of temperature, are an increase in the general absorption over a wide range of the spectrum, which decreases the number of bands in parts of the spectra which are unaffected in the *meta*-xylene. The merging of the narrow bands in the different parts of the spectra of the three isomers is evidently connected with the positions in the benzene ring where substitution of CH_3 for hydrogen has been effected.

It is proved that benzene vapour at 100° C. has the same molecular mass as at 25° C. or 12°·7 C., so that at lower temperatures the molecules are not associated when in a state of vapour.

The absorption bands at 100° C. are seen on comparison to be almost identical with those at lower temperatures, but at 100° C. there is this difference, that the bands in the region about λ 2700 are of augmented intensity, with a peculiar sharpness and definition which is wholly wanting at lower temperatures, as they then appear feeble and ill defined, or do not appear at all.

The similar groups of bands occurring in benzene and toluene, and the close similarity between the spectra of toluene and ethylbenzene, with the further resemblance between meta-xylene, toluene, and ethylbenzene, is evidence that the peculiar mode of vibration of the benzene nucleus, or ring-structure, is in a great measure unaffected by the side chain substitution in these compounds.

The important influence of the position of the substituted hydrogen in benzene upon the number and position of bands in the spectra of the homologues is clearly demonstrated.

The general absorption observed in *solution spectra*, like that in *vapour spectra*, is also apparently caused by the translatory motion of the molecules. The selective absorption, consisting of the coalescence of several narrow bands, is regarded as due to the intra-molecular motions; motions of the atoms, or atom-complexes, within the molecules, upon which, if the solution be concentrated, a general absorption is superposed. These observations are in accord with the conclusions arrived at in 1882 and 1885 upon evidence derived from the examination of solution spectra.

DESCRIPTION OF PLATES.

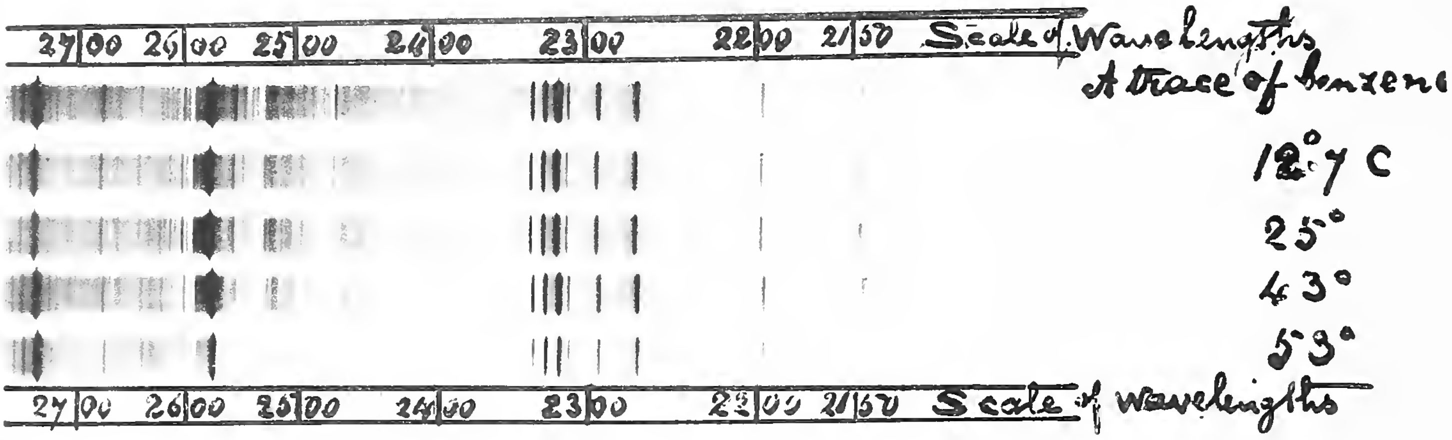
PLATES 32 AND 33.

The original photographs were taken on plates measuring 5 × 4 inches, on which the continuous rays and the cadmium lines appear dark. Good examples are figs. 6 and 7, where the cadmium spectrum is shown at the head of each series. The reproductions are from negatives slightly enlarged to about one and a half times the size of the originals.

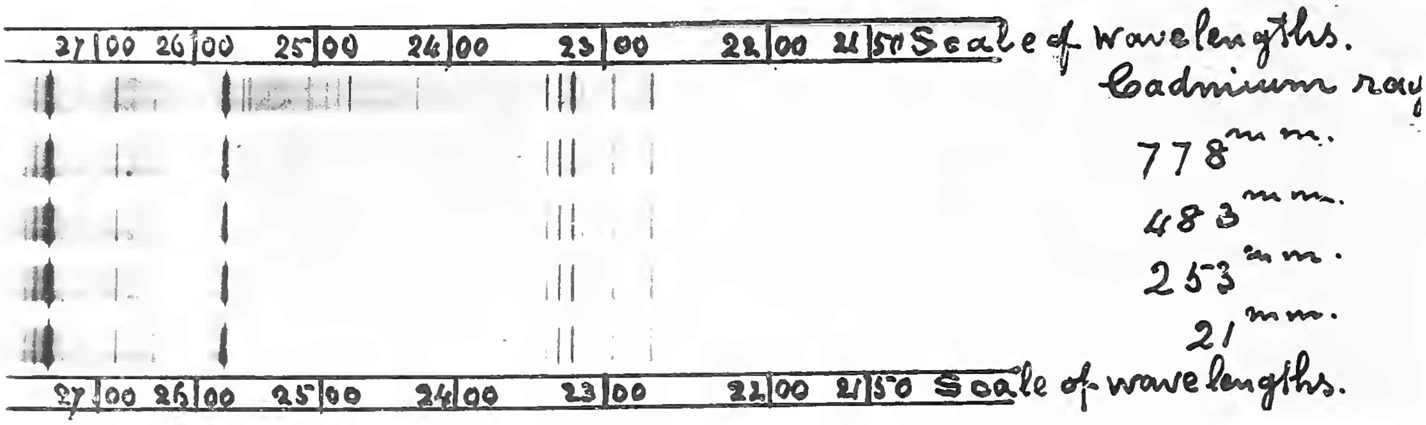
Particulars of figures will be found facing the plates.

The emission spectrum being dark the absorption bands appear white, or approaching to whiteness, according to whether they are strong or weak bands. On figs. 1 and 4 it will be seen that instead of the pure emission spectrum appearing at the head of the series a trace of benzene vapour gained access to the tube interposed between the spark and the slit of the spectrograph, when air was passed into it, and the absorption bands due to this trace of benzene are very distinctly shown. The reproductions do not compare in delicacy with silver prints taken from the original negatives, owing to a granulation resembling that of a lithograph, which somewhat impairs their definition.

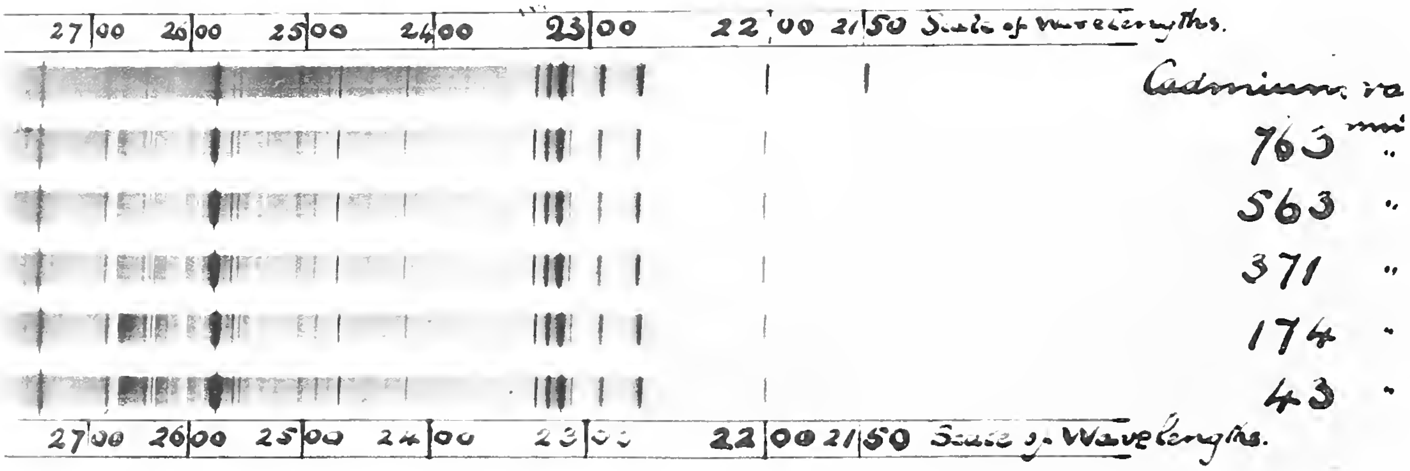
1


2700 2600 2500 2400 2300 2200 2150 Scale of Wavelengths
A trace of benzene
12°·7 C
25°
43°
53°
2700 2600 2500 2400 2300 2200 2150 Scale of wavelengths

2


2700 2600 2500 2400 2300 2200 2150 Scale of wavelengths.
Cadmium ray
778 mm.
483 mm.
253 mm.
21 mm.
2700 2600 2500 2400 2300 2200 2150 Scale of wavelengths.

6


2700 2600 2500 2400 2300 2200 2150 Scale of wavelengths.
Cadmium ra
763 mm
563
371
174
43
2700 2600 2500 2400 2300 2200 2150 Scale of Wavelengths.

7

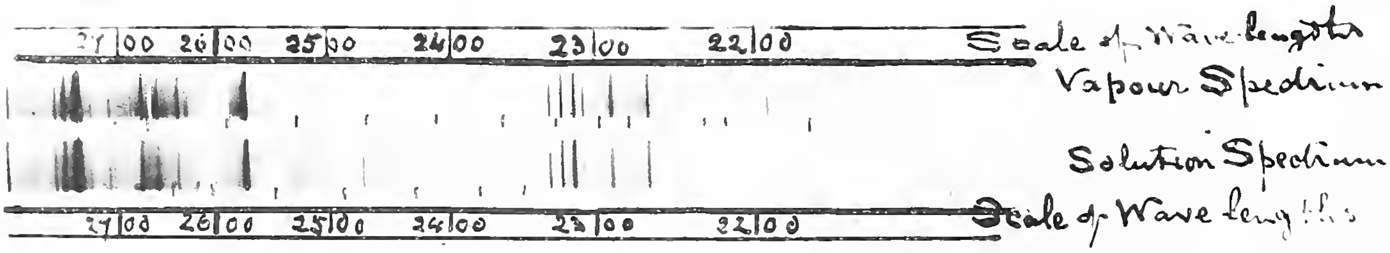

2700 2600 2500 2400 2300 2200 Scale of Wavelengths
Vapour Spectrum
Solution Spectrum
2700 2600 2500 2400 2300 2200 Scale of Wave lengths

PLATE 32.

Fig. 1. Four spectra of benzene at a pressure of 759·5 mm., and at different temperatures, varying from 12°·7 C. to 53° C. This series of photographs shows the head of a group of bands, being a narrow and somewhat feeble band, which is succeeded by a very strong band, about λ 2540 at 12°·7; it increases in strength down to 53° C. On the original plate bands are also seen about λ 2280, λ 2300, λ 2330, λ 2350, at 25° C., 43° C., and 53° C. For details see Table I., pp. 490–493.

Fig. 2. Four spectra of benzene at pressures varying from 778 mm. to 21 mm., and at a constant temperature of 11°·5 C., see Table II., pp. 493, 494. The original plate is an exceedingly delicate one, very difficult to reproduce and impossible to render satisfactorily. The head of the group at λ 2540, a narrow band, is very distinctly seen on the silver print of each of these spectra, but is very imperfectly shown on the reproduction.

Fig. 6. Five spectra of toluene at different pressures and a constant temperature of 11° C. Table IX., p. 509.

Fig. 7. The vapour-spectrum and solution-spectrum taken from the same quantity of benzene, and at the same time, for comparison. See pp. 519, 520. Bands and the heads of groups of bands are indicated by marks below the two spectra. They are well seen on the original plates, although not all visible on the reproductions.

PLATE 33.

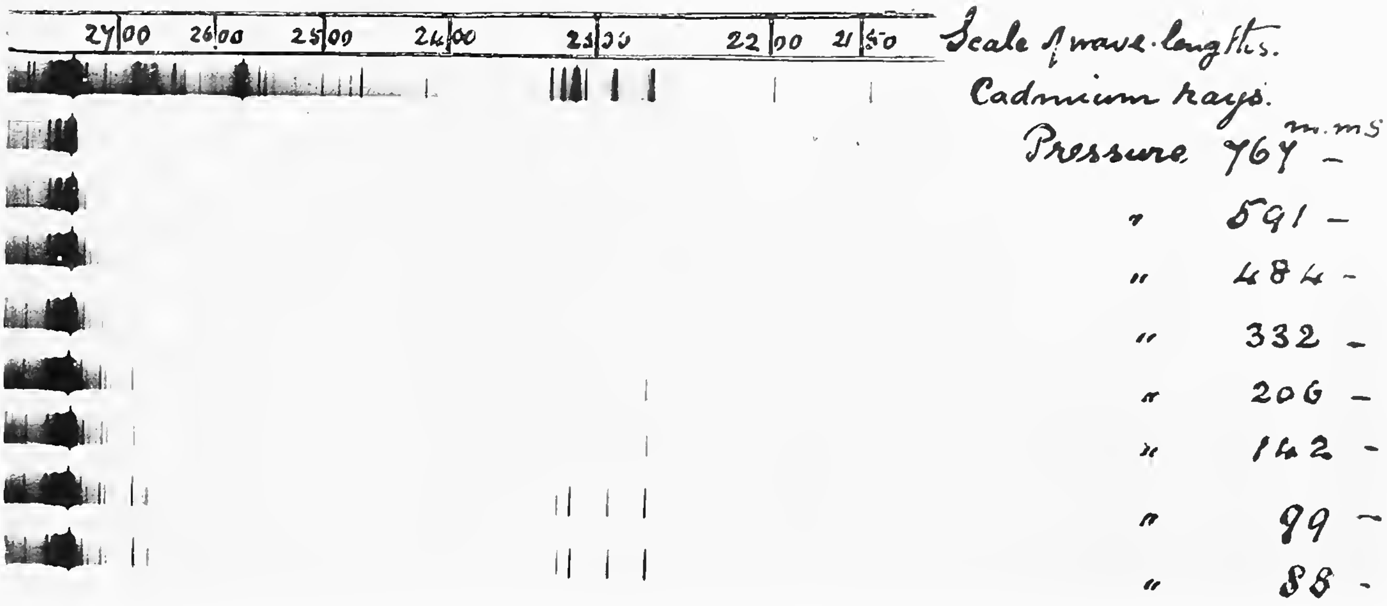
Figs. 3 and 4. Seventeen spectra of benzene vapour at different pressures, varying from 767 mm. down to 4·mm., at a constant temperature of 100° C., in a column 150 mm. long. These two series of spectra, the one in continuation of the other, show completely what was only indicated on fig. 2. See Table IV., p. 496, and Table VI., pp. 498–505.

On fig. 3, the least refrangible group of bands is well shown about λ 2700, at 484 mm. pressure, and continues to 88 mm.

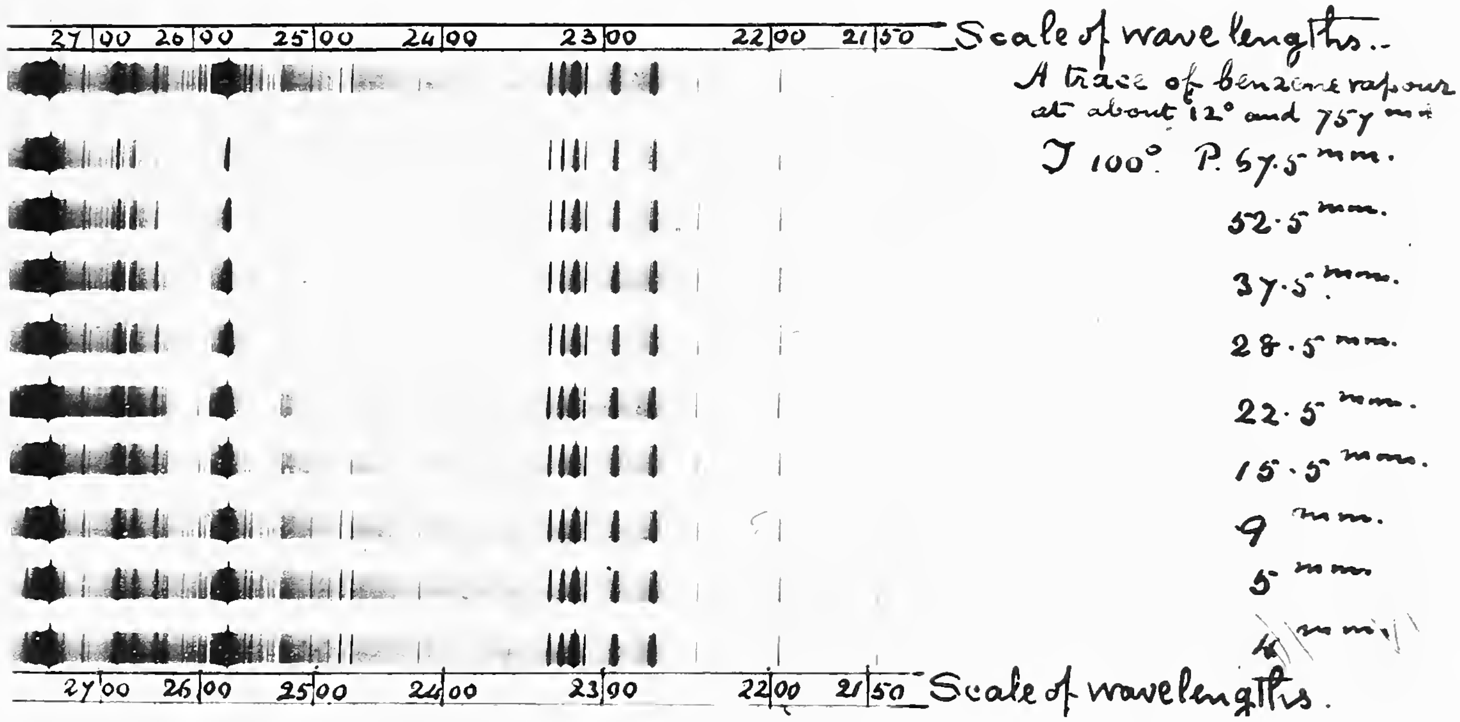
On fig. 4, the bands about λ 2700 are strong at pressures from 67·5 mm. to 28·5 mm. At the latter pressure the bands at λ 2600 become well defined. From 67·5 mm. to 22·5 mm. the bands at λ 2280, and near to λ 2300 are visible.

Fig. 5. This is a very fine series of spectra of toluene vapour at nine different temperatures from 10° C. to 100° C., and at a constant pressure of 751 mm., in a column 150 mm. long. See Table VIII., pp. 507, 508.

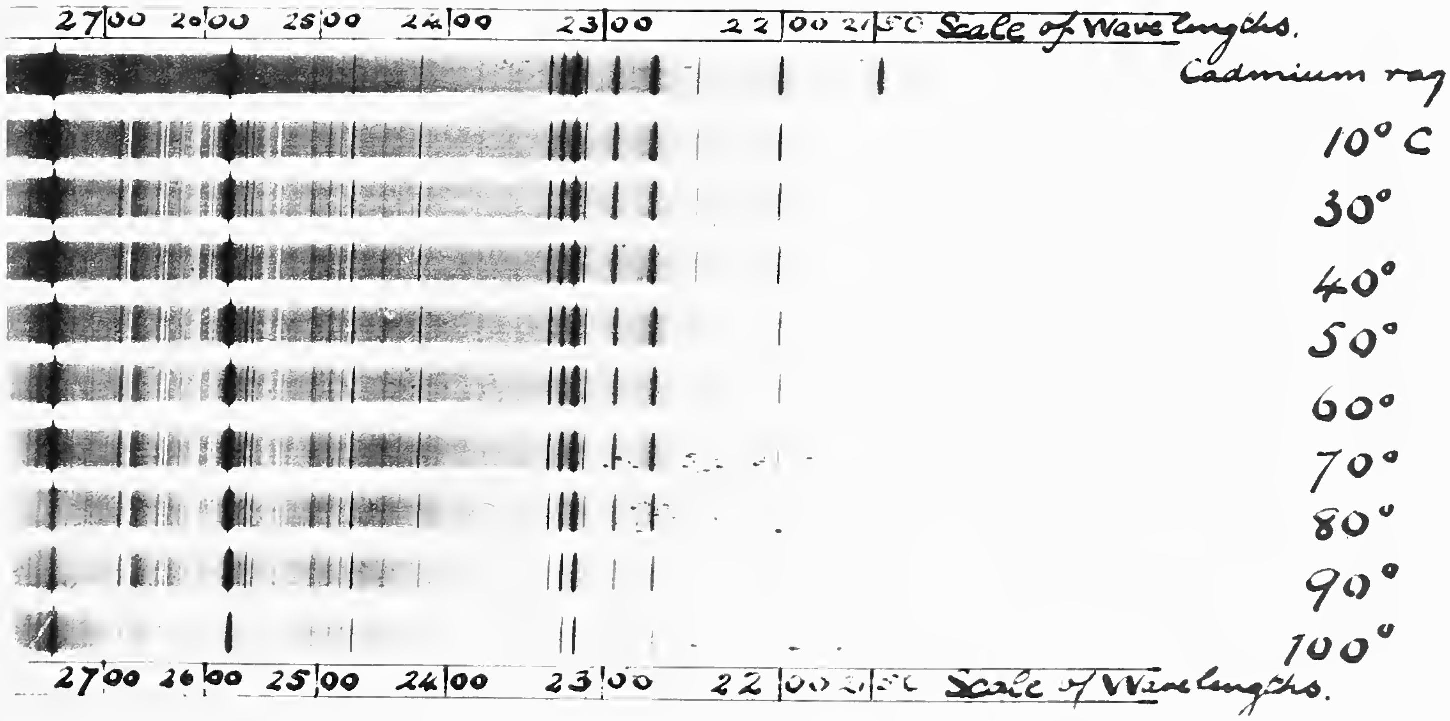
3


2700
2600
2500
2400
2300
2200
2150
Scale of wave lengths.
Cadmium rays.
Pressure 767 m.ms
" 591
" 484
" 332
" 206
" 142
" 99
" 88

4


2700
2600
2500
2400
2300
2200
2150
Scale of wave lengths..
A trace of benzene vapour at about 12° and 757 mm
T 100° P. 67.5 mm.
52.5 mm.
37.5 mm.
28.5 mm.
22.5 mm.
15.5 mm.
9 mm.
5 mm.
4 mm.
Scale of wavelengths.

5


2700
2600
2500
2400
2300
2200
2150
Scale of Wave lengths.
Cadmium ray
10° C
30°
40°
50°
60°
70°
80°
90°
100°
Scale of Wavelengths.

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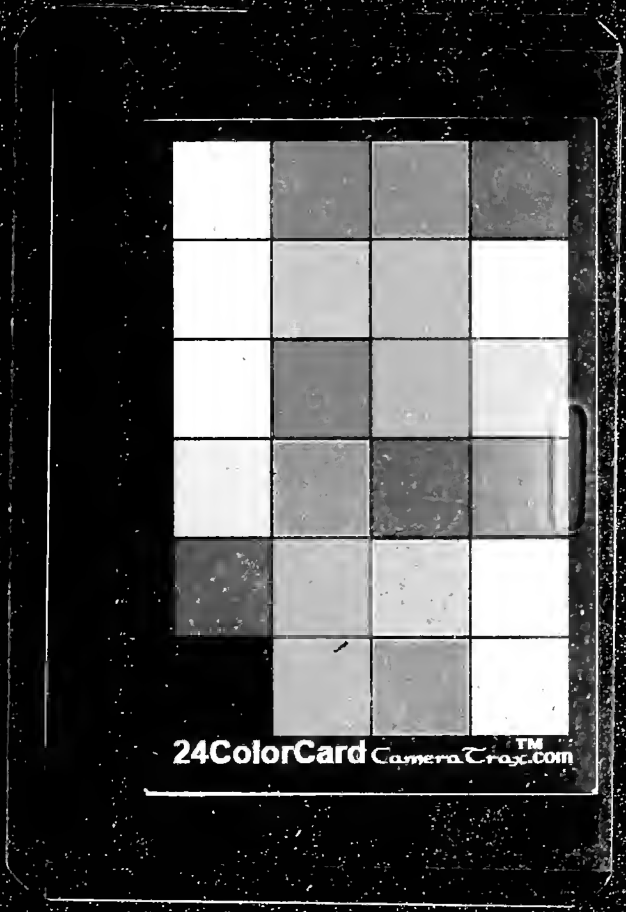
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