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KONINKLIJKE AKADEMIE
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-- TE AMSTERDAM --

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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XXV

N^{os}. 1 and 2.

President: Prof. F. A. F. C. WENT.

Secretary: Prof. L. BOLK.

(Translated from: "Verslag van de gewone vergaderingen der Wis- en
Natuurkundige Afdeeling," Vol. XXXI).

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Physics. — “A remarkable case of quantization.” By Prof. P. EHRENFEST and G. BREIT.

(Communicated at the meeting of January 28, 1922).

1. It is possible to indicate simple mechanical systems for which a formal application of the quantum rules gives well defined and yet apparently unreasonable stationary motions. BOHR'S Principle of Correspondence¹⁾ offers an essentially new viewpoint for the treatment of these cases and will probably contribute to their complete solution. It will suffice to discuss a special case which is so chosen as to minimize the mathematical analysis.²⁾

2. A rigid electric dipole having a moment of inertia I is free to rotate in the X, Y plane about its own midpoint.

Let us suppose that by means of a suitable kinematical arrangement the rotating dipole is thrown back elastically as soon as the angle φ , which the dipole makes with the axis of X , reaches the boundaries of the interval

$$-f \cdot 2\pi \leq \varphi \leq +f \cdot 2\pi \quad (1)$$

where f is a large, in general an irrational number. Let an angular velocity ω be given to the dipole. Its angular momentum is then $p = I\omega$ and it executes a periodic motion with the period

$$T = 4f \cdot \frac{2\pi}{\omega} \quad (2)$$

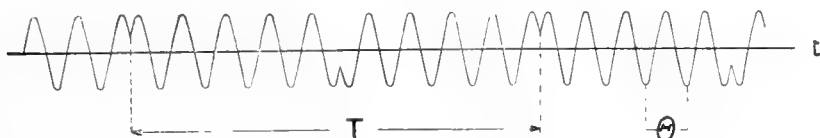
During the motion the dipole traverses the interval (1) making in a period $2f$ complete revolutions to the right followed by the same number of revolutions to the left. In the motion the “quasi-period”

¹⁾ N. BOHR, Quantum theory of line-spectra I, II Kopenhagen 1918. H. KRAMERS, Intensities of spectral lines. Kopenhagen 1919.

²⁾ A case which differs slightly from the one discussed in § 2, namely the case of a rigid dipole torsionally suspended by an elastic thread of small rigidity one of us submitted to EINSTEIN for consideration as early as 1912 (with reference to the problem of quantization of H_2 molecules — P. EHRENFEST, Verh. d. D. Phys. Ges. 15, 451, 1913). It was impossible however to settle the difficulty here discussed by the means which were then available.

$$\theta = \frac{2\pi}{\omega} \dots \dots \dots (3)$$

becomes noticeable. This period is a $4f^{\text{th}}$ part of T and is equal to the time taken by the dipole to make a complete revolution through the angle 2π . The projection of the moment of the dipole on a line in the plane $X-Y$ -say on the axis of X depends on the time in the manner shown on the figure (for the sake of economy the "large number" f is here taken as being approximately 2).



3. The quantum relation for our system is

$$\int p dq = nh \quad (n = 0, 1, 2 \dots) \dots \dots (4)$$

where the coordinate q is the angle φ , p is the corresponding momentum $l \omega$ and the integral is taken over a complete period T . This gives in our case

$$4f \cdot 2\pi p = nh \dots \dots \dots (5)$$

or

$$p = n \frac{h}{8f\pi} \dots \dots \dots (6)$$

If now the restricting boundary of the interval (1) is so chosen as to make f very large, then the differences between consecutive values of p (see (6)) (and therefore also between consecutive values of the energy) are very small.

4. This result appears to be unacceptable. In fact if we pass to the limit of $f = \infty$ i.e. if the restriction of the boundaries on the dipole disappears then equation (4) gives certainly

$$p = m \frac{h}{2\pi} \dots \dots \dots (7)$$

for now θ is the period. Here (Equ. (7)) p changes by finite steps whereas if the previous consideration be applied (Equ. (6)) the steps become infinitesimal for $f = \infty$. This is the contradiction to be discussed.

5. BOHR's principle of correspondence offers a new point of view for the treatment of this case. As before let f be a very large

number and suppose that the permissible values of p are truly given by Eq. (6). We want to know the requirements made by the principle of correspondence as to the "probability of a transition" from the state $n = n_1$ to the state $n = n_2$ (say as the result of absorption in a field of radiation). The Principle of correspondence regards the probability of the transitions as analogous to the amplitudes of "corresponding" harmonics in a Fourier series expansion of the function represented graphically on the figure. This function represents the dependence on the time of the X or Y component of the dipole's moment. The Fourier expansion of the function may be put into the form

$$X = \sum_1^{\infty} A_s \cos \left(s \frac{2\pi}{T} \right) \dots \dots \dots (8)$$

The harmonics "corresponding" to the transition $n_1 \rightarrow n_2$ are given by:

$$s = n_2 - n_1 \dots \dots \dots (9)$$

From an inspection of the figure or by means of a short calculation it becomes apparent that for a large value of f the amplitudes of all the harmonics are small with the exception of those harmonics whose period is nearly equal to the "quasiperiod" θ i.e. with the exception of those for which

$$\frac{T}{s} \cong \theta \dots \dots \dots (10)$$

or

$$s \cong 4f \dots \dots \dots (11)$$

Therefore if f is large all the transitions have a very small probability with the exception of those for which very nearly

$$n_2 - n_1 \cong 4f \dots \dots \dots (12)$$

and therefore (in virtue of (6))

$$p_2 - p_1 = (n_2 - n_1) \frac{h}{4f \cdot 2\pi} \cong \frac{h}{2\pi} \dots \dots \dots (13)$$

which is the same as the interval between consecutive values of p prescribed by (7) for infinitely large values of f .

6. If therefore we should take a collection of identical samples of our system having all the same *very large value of f* , being all at rest i.e. in the state $p = 0$ at the time $t = 0$ and if we should subject each sample independently to the action of a black body radiation — then we should find at a later time t that:

A. Out of the very dense succession of the p levels which are

permitted by (6) only those are occupied by an appreciable number of the systems which nearly coincide with the levels of p given by (7).

B. The transitions which take place have almost without exception the magnitude $\frac{h}{2\pi}$ (and not a multiple of it) (See (13)). This is again in good agreement with the fact that for $f = \infty$ the FOURIER expansion of the x (or y) component contains only the fundamental and no higher harmonics so that for this case the Principle of Correspondence allows only the transitions (see (7)) for which $m_2 - m_1 = \pm 1$.

7. A question must now be mentioned the precise explanation of which would be of value. For the discussion of thermal equilibrium in our complex we must know the "weights" (the *a priori* probability) to be ascribed to each p level. For $f \pm \infty$ it would appear that the same weight should be given to every stop of (6) — independently of the value of f and independently of the density with which the levels follow each other. On the other hand for $f = \infty$ only the levels given by (7) are to have a weight (the same for all). A closer examination of this case will probably make it necessary to consider the fact that we are concerned here with a double limit viz. $\lim t = \infty$ (the lapse of an infinitely long time for the establishment of thermal equilibrium) and $\lim f = \infty$; our dissatisfaction is really based on an unconscious demand that the result should be independent of the order in which the two limits are approached.

The junior author of the paper (G. BREIT) is Fellow of the National Research Council, United States of America.

The University, Leiden.

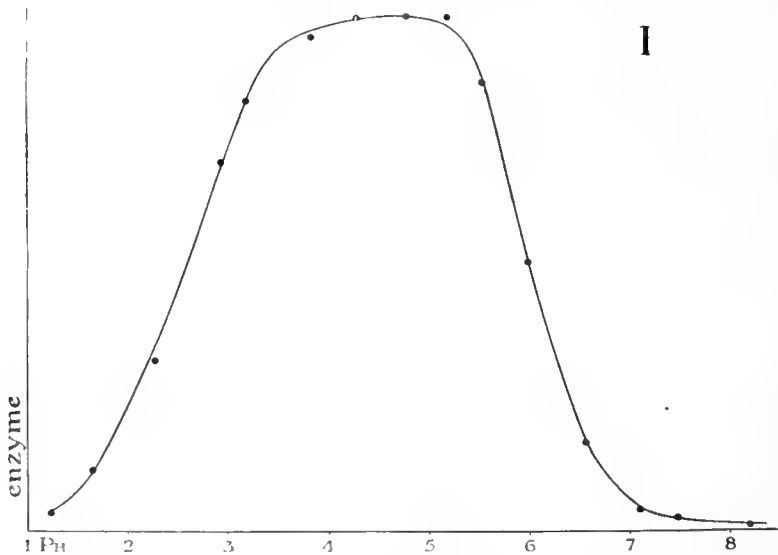
Botany. — “*The influence of hydrogen ion concentration upon the action of the amylase of Aspergillus niger*”. By G. L. FUNKE.
(Communicated by Prof. F. A. F. C. WENT).

(Communicated at the meeting of January 28, 1922).

Aspergillus niger produces large quantities of amylase, part of which migrates into its nutritive surrounding. In the mean time the fungus forms acids which cause that medium to have a high hydrogen ion concentration. As this however seemed not to influence unfavourably the action of the amylase, the supposition was justified that the amylase of *Aspergillus niger* could not have its optimal action at the same hydrogen ion concentration as the ptyaline which works best at a nearly neutral or faintly acid reaction (4 and 5).

Therefore I made a preliminary investigation in the way as has been indicated first by SÖRENSEN (1). Buffer solutions however were made according to the methods of CLARK and LUBS (7).

Generally the same amounts of enzyme solution out of the nutritive liquid were mixed up with buffer solution and amylum



solution 0.16%. The hydrogen ion concentration of this mixture was determined by aid of colorimetric indicators, the rate of hydrolysis of the amylum by the iodine reaction.

Results are plotted into the annexed curve (I). As can be seen there is no point of optimal action but a broad optimal zône extending from a P_{H} of about 3,5 till about 5,5.

Neither the concentration of the amylase, nor the composition of the nutritive liquid appeared to have influence. The same results were obtained with amylase extracted from the mycelium.

These results largely confirm the theory of MICHAËLIS who considers the enzymes as ampholytes (2 and 3). The form of the curve indeed is nearly identical to the dissociation rest curve of an amphotere electrolyte. According to his formulas

$$\varrho_a = \frac{1}{1 + \frac{K_a}{(H)}} \quad \text{and} \quad \varrho_b = \frac{1}{1 + \frac{K_b}{(OH)}}$$

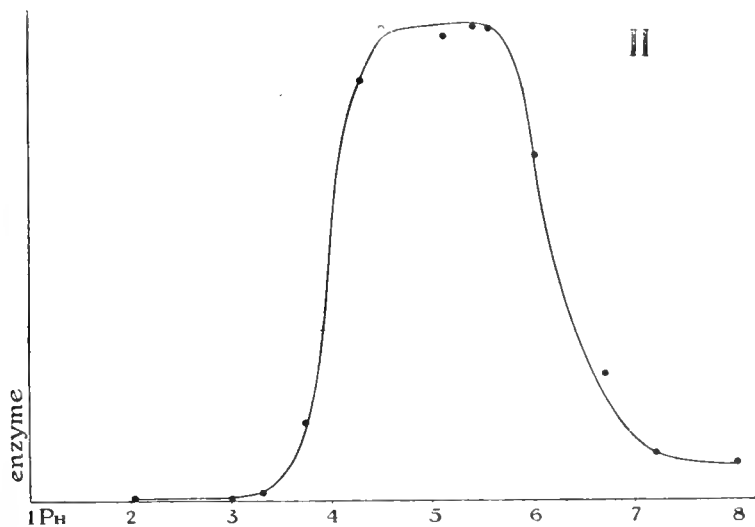
in which $\varrho = 1 - \gamma =$ dissociation rest

$\gamma =$ rate of dissociation

$K_a =$ dissociation constant of the acid

$K_b =$ dissociation constant of the base

the points on the ordinate = half of the maximum height of the curve indicate the logarithms of the dissociation constants of acid and base on the abscissa. These are to be found at about 2,26 and 6,2. So the dissociation constant of the acid would be $= 6.3 \times 10^{-7}$, that of the base $= 2.884 \times 10^{-12}$.



We may consider in the same way curve II which represents

the influence of the hydrogen ion concentration upon the amylase of malt¹⁾.

The dissociation constant of the acid appears to be the same as for the amylase of *Aspergillus*, that of the base on the contrary is bigger i.e. $= 5.76 \times 10^{-11}$. So as an acid the two amylases are equally strong, as a base that of the malt is the weakest.

Further investigations on other sorts of amylase will perhaps instruct us, if pointing out their differences in this way will be of any value.

Utrecht, November 1921.

Botanical Laboratory.

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¹⁾ It might be doubted if the iodine reaction method is accurate enough to get exact results. I therefore refer to those of ADLER (6) who determined the hydrolysis of amylum by means of rotation and reductive power. The numbers he obtained appear to give a curve nearly identical to mine.

Palaeontology. — “*Ueber einen fossilen Baumstamm von Bolang (Java), ein Beitrag zur Kenntnis der fossilen Flora Niederländisch-Indiens*”. By Dr. R. KRÄUSEL. (Communicated by Prof. J. W. MOLL.)

(Communicated at the meeting of January 28, 1922).

In der Sammlung des Mineralogisch-Geologischen Instituts der Reichsuniversität zu Groningen befindet sich ein äusserlich sehr gut erhaltenes Stück eines verkieselten Baumstammes von Bolang auf Java. Der Durchmesser des 23 cm langen Bruchstückes beträgt 19—23 cm. Ueber Fundort u.s.w. gibt folgende Notiz Auskunft: „Fossiler Baumstamm (batoe sempoe), wie solche in verschiedener Grösze, bis 2 m lang und mit einem zuweilen 60 cm erreichenden Durchmesser in Bolang auf Java gefunden werden. Sie kommen häufig auf der Oberfläche oder im Flussbette zerstreut vor, finden sich aber auch in 1—2 m Tiefe im Boden auf dem Kamm eines Hügelzuges. (Empfangen von Herrn C. BARENDS)”. Angaben über das geologische Alter der Fundschicht liegen nicht vor.

Der von Herrn Prof. Dr. BONNEMA, dem an dieser Stelle zu danken, mir eine angenehme Pflicht ist, ausgehenden Anregung zur Untersuchung des Holzes leistete ich um so lieber Folge, als es wünschenswertes Vergleichsmaterial für eine gleichzeitig durchgeführte Bearbeitung fossiler Hölzer aus Sumatra bot, über die an anderer Stelle berichtet wird (KRÄUSEL 1). Dort ist auch zu zeigen versucht worden, dass die Behandlung derartiger Reste keineswegs nutzlos ist, selbst angesichts der zum Teil noch recht unvollkommenen Kenntnis vom anatomischen Bau der rezenten, tropischen Laubbäume. Gerade dieser Umstand verlangt aber eine möglichst ausführliche Beschreibung der Fossilien. Nur dann ist eine brauchbare Grundlage für eine etwa später vorzunehmende kritische Revision gegeben. Aus diesem Grunde wurde die Beschreibung der von MOLL und JANSSONIUS (1) in die Literatur eingeführten Methode angepasst, soweit dies angesichts des Erhaltungszustandes der fossilen Hölzer eben möglich war. Das soll auch hier geschehen; hinsichtlich aller Einzelheiten kann auf die schon genannten Arbeiten verwiesen werden.

Beschreibung des anatomischen Baues (Topographie):

Zuwachszonen mit freiem Auge kaum sichtbar, unter dem Mikroskop an einer deutlichen Anhäufung und damit verbundenen Gröszenabnahme der Gefässe kenntlich. Die tangentialen Schichten, die

auf dem Querschnitt für das blosse Auge Zonengrenzen ähnlich sind, enthalten zahlreiche, stets von reichlichem Holzparenchym umgebene Harzgänge und auch Gefäße, aber fast kein Libriform. Diese Schichten nicht überall gleich deutlich, stets eine Reihe Harzgänge enthaltend, von denen 2 benachbarte zuweilen verschmelzen (auf 18 mm radialer Erstreckung kommen 5 Harzgangreihen, die sich über einen grossen Teil des Querschnitts verfolgen lassen). (Textfig. 1, Tafel, Fig. 1, 2). Gefäße \pm gleichmässig verteilt, zu 8—16 auf dem mm²,

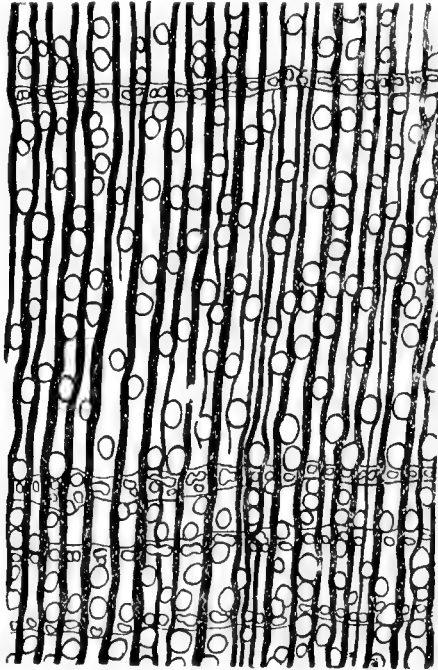


Fig. 1. Querschnitt.

in der Regel vereinzelt liegend, seltener in Gruppen, dann oft zu zweien. Sehr oft an beiden oder wenigstens an einer Seite an Markstrahlen grenzend, sonst meist von Holzparenchym oder Fasertracheiden umgeben. Diese sehr spärlich, nur an Gefäße grenzend. Libriformfasern die Grundmasse des Holzes bildend, \pm undeutlich in radialen Reihen angeordnet.

Einfaches Holzparenchym die Gefäße und Harzgänge umgebend, tangentielle Bänder bildend, einige zerstreute Fasern anscheinend auch im Libriform eingesprengt; die die Harzgänge umgebenden Zellen oft in die Breite gezogen, kaum in den Harzgang hineinragend (dünnwandiger als die anderen). Harzgänge nur in den tangentialen Bändern zahlreich, ausserhalb derselben nur vereinzelt. Markstrahlen seitlich von einander getrennt durch 1—10 Libriformfaserreihen, 1—6-

am häufigsten 3—5-schichtig, 3—30 Zellen hoch, die breiteren nicht immer aus 3 Stockwerken zusammengesetzt, das obere und untere dann meist eine, seltener bis 4 Zellen hoch, die wie die der einfachen Markstrahlen aufrecht oder aufrechten ähnlich sind. Die breiteren Stockwerke oft von tangential häufig sehr breiten Hüllzellen umgeben. Nicht selten stehen mehrere Markstrahlen, nur durch ein oder zwei Fasern von einander getrennt, übereinander, verschmelzen auch gelegentlich ganz (Tafel, Fig. 3; Textfig. 2). Ihre Zellen enthalten oft Kristalle.

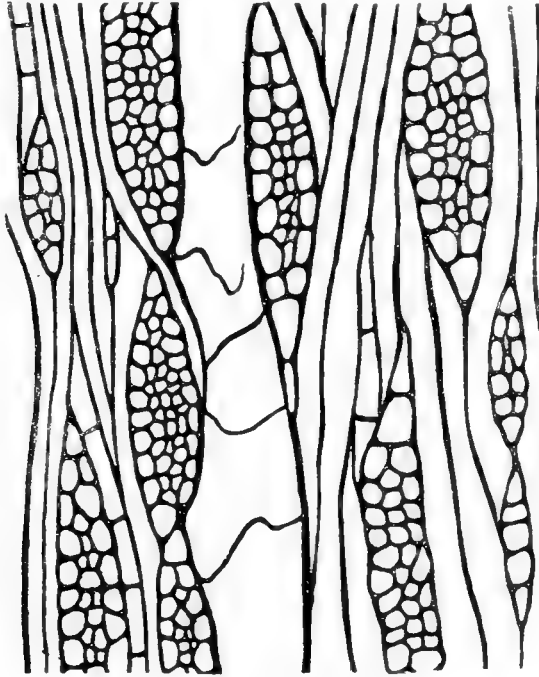


Fig. 2. Tangentialschnitt.

Beschreibung der Elemente:

Gefäße: Weite radial $65\text{--}275\ \mu$, tangential $70\text{--}210\ \mu$, elliptische, auch Kreiszyylinder, Querwände \pm horizontal (selten sichtbar), Perforation \pm unkenntlich (lochförmig?) mit zahlreichen Hoftüpfeln, wo sie aneinander oder an Fasertracheiden grenzen, Tüpfel polygonal-rundlich oder elliptisch; die Pori oft elliptisch, schief bis vertikal gestellt; mit einseitigen Hoftüpfeln und einfachen Tüpfeln, wenn an Holzparenchym und Markstrahlen grenzend, häufig mit dünnwandigen Thyllen erfüllt.

Fasertracheiden: Nur in der Umgebung der Gefäße vorhanden, Tüpfelung wie bei den Gefäßen.

Libriformfasern: Weite radial $8\text{--}16\ \mu$, tangential $10\text{--}16\ \mu$,

polygonal mit oft abgerundeten Kanten, oft auch vierseitig. Tüpfel spaltenförmig, seltener auch rundlich. Interzellularräume wurden nicht beobachtet.

Holzparenchymzellen: Weite radial 10—35 μ , tangential 10—30 μ , Länge 40—200 μ , 4—8-seitige Prismen mit abgerundeten Kanten und vertikaler Achse, die Zellen um die Gefäße und namentlich um die Harzgänge oft in die Quere gezogen, mit einfachen Tüpfeln, wo sie aneinander und an Markstrahlen grenzen, im übrigen vgl. das bei den Gefäßen bzw. dem Libriform gesagte. Die Tüpfel oft auf der Radialwand in 1 oder 2 vertikalen Reihen angeordnet. Interzellularen nicht erkennbar.

Harzgänge: Weite radial 30—90 μ , tangential 30—80 μ , darin gelegentlich braune Harztropfen.

Markstrahlzellen:

1. Liegende: Weite radial 30—80 μ , tangential 7—20 μ , Länge 10—40 μ , polygonale Prismen mit radialer Längsachse und abgerundeten Kanten, die tangentiale Wand meist senkrecht stehend, getüpfelt wie die Parenchymzellen.

2. Aufrechte: Weite radial 30—60 μ , tangential 10—20 μ , Länge 20—60 μ , mit längsgerichteter Achse, im übrigen wie die liegenden Zellen. Inhalt fast stets Harz, ausserdem sehr oft in den aufrechten, aber zerstreut auch in Hüllzellen und liegenden Zellen ein deutlicher, meist \pm kleiner Einzelkristall, der in der Regel nur einen Teil des Zellinneren ausfüllt (Tafel, Fig. 4, 5).

Bestimmung des Holzes:

In der Beschreibung fehlen, gemessen an der „Linnean Method“ von MOLL und JANSSONIUS, viele Einzelheiten. Das ist eine Folge der zum Teil mangelhaften Erhaltung des Fossils. Dennoch ist eine Bestimmung durchaus möglich. Charakteristische Merkmale sind die Markstrahlen, das Parenchym und die Harzgänge, die erkennen lassen, dass in dem Holz eine Dipterocarpaceenart vorliegt. Solche waren auch unter dem Djambimaterial (KRÄUSEL 1) häufig; sie sind als *Dipterocarpoxyylon Tobleri*, *Dipterocarpoxyylon* sp. (? *Tobleri*) und *Dipterocarpoxyylon* sp. beschrieben worden. Dazu tritt noch *Dipterocarpoxyylon burnense* HOLDEN, und es konnte schliesslich gezeigt werden, dass auch *Grewioxylon Swedenborgii* SCHUSTER sowie *Woburnia Scottii* STOPES zu *Dipterocarpoxyylon* gestellt werden müssen, von denen die erste Art *Dipterocarpoxyylon Tobleri* recht nahe steht, aber höhere Markstrahlen und gefächertes Holzparenchym besitzt.

Sehen wir von *Dipterocarpoxyylon Scottii* aus der unteren Kreide Englands ab, das wegen seiner anders verteilten Harzgänge und der im übrigen \pm mangelhaften Erhaltung für den Vergleich mit dem

vorliegenden Fossil nicht in Frage kommt, so sind alle diese Hölzer auf Südostasien beschränkt. Mit keinem kann das Holz von Bolang vereinigt werden. *Dipterocarpoxyton burmense* besitzt einreihige Markstrahlen, *Dipterocarpoxyton* sp. viel grössere Gefässe und häufigeres zerstreutes Parenchym, *Dipterocarpoxyton Swedenborgii* viel höhere Markstrahlen (bis 80 Zellen hoch) und teilweise gefächertes Parenchym. *Dipterocarpoxyton Tobleri* schliesslich stimmt in allgemeinen zwar mit unserem Holz gut überein, doch ergeben sich für dieses folgende Unterschiede: Alle Elemente sind relativ viel kleiner, das wird vor allem deutlich bei Gefässen, Harzgängen, Höhe und Breite der Markstrahlen. Wenn auch diese Verhältnisse innerhalb einer Art individuellen Schwankungen ausgesetzt sind, so dürften derartige Unterschiede (die Weite der Harzgänge z. B. bei *Dipterocarpoxyton Tobleri* 100—300 μ , hier nur 30—90 μ), wo es sich doch unzweifelhaft um altes Stammholz handelt, systematisch bedingt sein. Namentlich der Tangentialschnitt mit den verhältnismässig viel breiteren Markstrahlen bietet ein ganz anderes Bild. Dazu kommt in den Markstrahlen das häufige Auftreten von Einzelkristallen, die *Dipterocarpoxyton Tobleri* ebenso wie anscheinend allen anderen bisher beschriebenen Formen durchaus fehlen. Dass es sich hierbei nicht um etwaige schlechte Erhaltung handeln kann, ist bereits betont worden (KRÄUSEL 1). Das vorliegende Fossil, dessen Gewebe viel schlechter erhalten ist als das eines Teiles der Djambihölzer, zeigt aufs Neue, dass gerade die Kristalle, wenn überhaupt vorhanden, auch sehr gut erkennbar bleiben.

Es ist eine neue Form, die als

Dipterocarpoxyton javanense

bezeichnet werden soll.

Mit einer bestimmten lebenden Art kann das Fossil bei dem derzeitigen Stande der anatomischen Holzuntersuchung kaum identifiziert werden. Es sei auf das an anderer Stelle gesagte (KRÄUSEL 1) verwiesen. Auszuschliessen dürfte die Gattung *Dipterocarpus* selbst sein, bei der die Markstrahlkristalle nach allen bisherigen Untersuchungen fehlen. Sie finden sich dagegen sicher bei Arten von *Hopea* und *Vatica*. Auch MOLL und JANSSONIUS (I I 347 u. f.) geben sie nur für *Hopea fagifolia* MIQ. und *Vatica bancana* SCHEFF. an, wo sie aber nur in den aufrechten Markstrahlzellen auftreten. Jedoch fehlen beiden Zuwachszonen und *Vatica bancana* auch die tangentialen Harzgangreihen, wozu noch manche kleinere Unterschiede kommen. Nach alledem handelt es sich bei dem Fossil also vielleicht um eine *Hopea*-oder *Vatica*-art. Gerade die Häufigkeit und

Verteilung der Harzgänge scheint ja ziemlich grossen Schwankungen innerhalb der einzelnen Gattungen zu unterliegen.

Die bisher bekannt gewordenen Dipterocarpoxylo sind tertiären Alters, und dies gilt wohl auch für *Dipterocarpoxylon javanense*. Kieselhölzer sind ja im Tertiär des ganzen Gebietes weit verbreitet, und schon GOEPPERT (1) hat solche in seiner Tertiärflora von Java abgebildet, ohne dasz allerdings seine Bilder eine Bestimmung der Hölzer ermöglichen würden.

Immer wieder zeigt sich also, dasz die Dipterocarpaceen auch im Tertiär in Südostasien weit verbreitet waren. Wir gehen daher in der Annahme kaum fehl, dasz sie schon damals eine ähnliche Rolle wie heute in der Flora des Gebietes gespielt haben, dasz diese also verhältnismässig geringe Veränderungen vom Tertiär bis zur Jetztzeit durchgemacht hat.

Zum Schlusse mögen noch die bisher bekannt gewordenen fossilen Dipterocarpaceenhölzer in Form einer Tabelle zusammengestellt werden.

DIPTEROCARPOXYLON HOLDEN.

| | | |
|--|---|---|
| 1. a) Markstrahlen ohne Kristalle | 2 | |
| b) Markstrahlen mit Kristallen | | <i>D. javanense</i> (Tertiär? Bolang, Java). |
| 2. a) Markstrahlen mehrreihig | 3 | |
| b) Markstrahlen einreihig | | <i>D. burmense</i> (Tertiär, Burma). |
| 3. a) Harzgänge in (±) langen tangentialen Parenchymbändern | 4 | |
| b) Harzgänge nur sehr zerstreut | | <i>D. Scottii</i> (untere Kreide, England). |
| 4. a) Neben den tangentialen Reihen auch zerstreute Harzgänge | 5 | |
| b) Neben den tangentialen Reihen keine zerstreuten Harzgänge | | <i>D. sp.</i> (Tertiär; Sumatra). |
| 5. a) Die tangentialen Harzgangreihen sehr lang | 6 | |
| b) Die tangentialen Harzgangreihen kürzer, oft unterbrochen | | <i>D. sp. (Tobleri?)</i> (Tertiär, Sumatra). |
| 6. a) Markstrahlen bis 80 Zellen hoch, die Einzelzellen bis 140 μ hoch (gefächertes Parenchym) | | <i>D. Swedenborgii</i> (Tertiär, Ostindien). |
| b) Markstrahlen bis 50 Zellen hoch, die Einzelzellen bis 90 μ hoch (einfaches Parenchym) | | <i>D. Tobleri</i> (Tertiär; Sumatra): |

Die Zahl der bisher untersuchten fossilen Hölzer des Gebietes ist angesichts der Häufigkeit ihres Vorkommens verschwindend gering, obwohl sie einen wesentlichen Beitrag zur Kenntnis der fossilen Flora liefern würden.

ABBILDUNGEN.

Textfig. 1. Querschnitt, Uebersichtsbild.

Tafel, Fig. 1. Desgleichen. Markstrahlen, Gefäße, tangentielle Holzparenchymbänder mit Harzgängen. ²⁵/₁.

Tafel, Fig. 2. Desgleichen. ⁵⁵/₁.

Tafel, Fig. 3. Tangentialschnitt. Verteilung der Markstrahlen. ²⁵/₁.

Textfig. 2. Desgleichen. ⁵⁰/₁.

Tafel, Fig. 4, 5. Radialschnitt. Aufrechte und liegende Markstrahlzellen, teilweise darin Harz und Kristalle. ¹⁵⁰/₁.

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Dezember 1921.

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Anatomy. — "*On the Significance of the Supra-orbital Ridges in the Primates.*" By Prof. L. BOLK.

(Communicated at the meeting of February 25, 1922).

The significance of any morphological feature may be gathered either from the function it performs, or from its mode of origin. Of these two methods it is always best to follow the first and to employ the second only when the first fails or yields unsatisfactory results. That the first method yields more reliable results is substantiated by the fact that in the application of this method direct observations are the basis for our conclusions, which in the other case are supported at best by more or less plausible reasoning and speculation about the possible influences and correlation of phenomena.

What I wish to state about the significance of the supra-orbital ridges in the Primates I have preceded by this contrast between the two methods of scientific morphological research, since not long ago the same subject was raised at one of our meetings by our fellow-member Prof. DUBOIS, who chiefly adopted the second method. I also propose to discuss the question of the supra-orbital ridges of the Primates — about which I pronounced my opinion on a previous occasion. However, in my discourse I will scrupulously keep within the bounds of immediate observation.

First of all let us consider the facts. When comparing the human skull with that of Anthropoids — to which group I will confine myself for the time being — we are struck at once by the difference in contour where the cerebral crane passes into the facial skull. That this difference is accentuated by the orthognathy of the human skull as contrasting with the marked prognathy of the Anthropoid skull, is only of secondary importance for our problem. The Anthropoid skull has no external frontal vault, which is the reason why some consider this skull to be flattened. This belief may be supported by the comparison of young Anthropoid skulls with those of adults. In the former the supra orbital ridges are absent, which makes the skull look much more like that of man. The ridges are formed as the ape grows up. This development commences shortly after the complete eruption of the milk set about the time when the first permanent molar appears.

Now what is the function of these supra-orbital ridges? To find the answer the researcher should ascertain the part played by these ridges in the structure of the skull as a whole, and what is their topographical relation to their immediate surroundings. This may be done quickest by making a sagittal section that extends along the axis of the orbit, through the ridge and the adjoining part of the skull. The image resulting from it is represented for Gorilla in fig. 1.

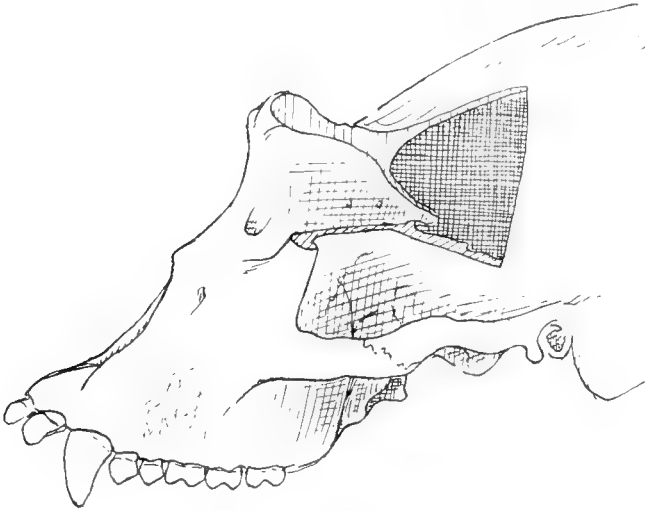
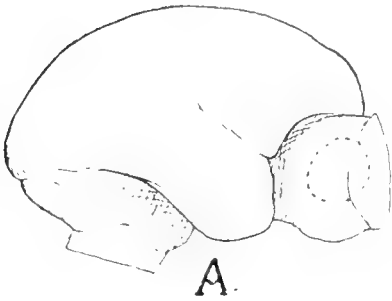


Fig. 1.

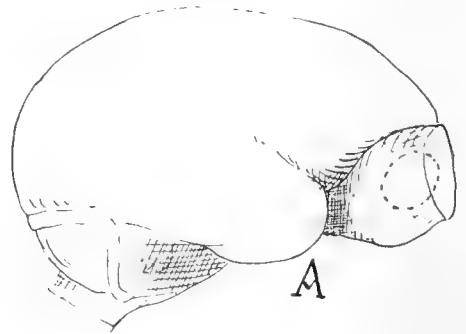
What does this figure teach us? First of all that, properly speaking, the term supra orbital ridge is not quite fit and that this formation cannot be compared with the occipital-, and the sagittal ridge also characterizing the skull of Gorilla. For, in reality, of this so-called supra-orbital ridge the lateral portions form the roof of the orbits, while the central part forms the roof of the nasal cavity. If, therefore, the supra-orbital ridge should be removed, nearly the whole content of the orbita would be deprived of the overlying osseous wall and would consequently come to lie immediately under the skin.

Direct observation of the topographical relation, therefore, leaves no manner of doubt about the function of the so-called supra-orbital ridge, it is namely the indispensable osseous wall of the orbita at the top. It is not a crest like the crista sagittalis and the crista occipitalis, but it is an indispensable wall of a cavity in the skull. But if this is a fact the origin of the superorbital ridge must be closely allied to general growth-phenomena of the skull after the early childhood of the ape. For we stated that, notwithstanding the absence of the supra-orbital ridges in the child-ape, still also here

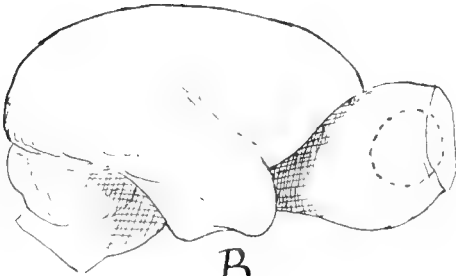
the orbita is provided with an osseous roof. It is a fact, indeed, that in this part of the skull radical changes have taken place in the topographical relations. These changes may be summarized as follows: in the child-anthropoid, and a fortiori in the fetus, the orbits are situated under the cranial cavity, whereas in the adult they are for the greater part precerebral. While they are lying under the cranial cavity the bottom of this cavity makes up the roof for the orbits, but when the orbitae are shifted precerebral a new roof is to be formed for an adequate protection of the contents. That we really have to do here with a displacement of the whole content of the orbita anteriorly and not with a simple enlargement of the orbitae, is illustrated by Figs 2 and the following. They represent casts of the cranial cavity and orbita, in situ.



A.

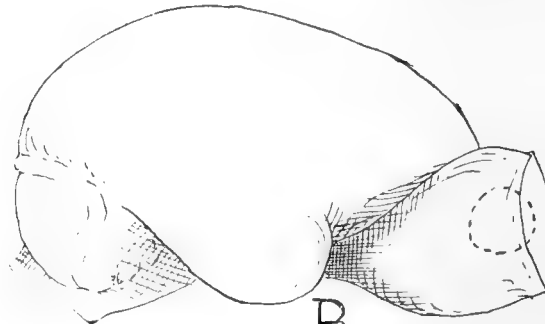


A.



B.

Fig. 2.



B.

Fig. 3.

These casts were made in the following way: Copper wire of adequate thickness was stuck through the communications between orbit and cranial cavity; subsequently the orbit and the cranial cavity were filled with plaster of Paris. Finally the enclosing skeleton was cautiously removed with a chisel. In this way an exact image is obtained of the topographical relations between the cranial cavity and the orbita.

Fig. 2A represents a cast of the cranial cavity and orbita of a young *Macacus cynomolgus*, Fig. 2B those of an adult specimen. A dotted line indicates the location of the eye-ball. When comparing the two figures, the difference between the young and the adult specimen as to topographical relation of the orbita and consequently of the eyeball, is quite obvious. In the young specimen the eyeball is still subcerebral, in the adult it is on the other hand precerebral.

The same holds for *Siamanga syndactylus*, though in a smaller degree than for *Macacus*, as will be seen in Fig. 3A (young animal) and 3B (adult). Here the anterior displacement of the orbit during growth is not so considerable as with *Macacus*, which accounts for

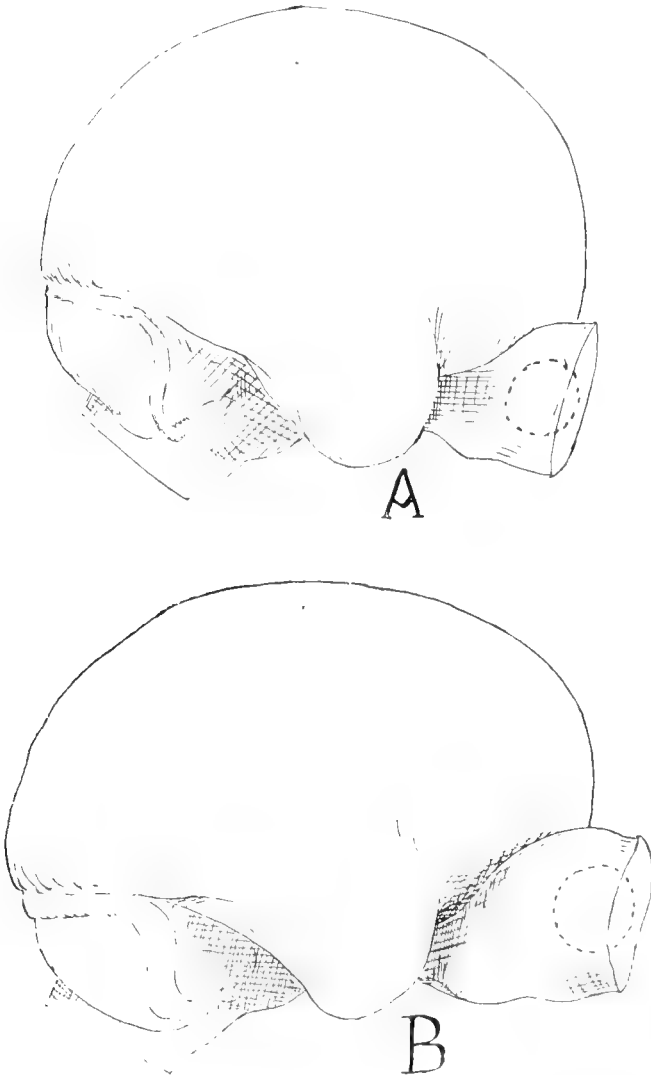


Fig. 4.

the fact that in Gibbon the so-called supra orbital ridge is less developed than in Macacus.

This is the case in a still smaller measure in Orang, as appears from a comparison between fig. 4A and 4B. Although we distinctly observe here an anterior shifting of the orbita, it is only slight. This is why in Orang no supra-orbital ridges have been developed, but only a general thickening of the frontal bone immediately over the orbitae.

A comparison of the figures 2, 3, and 4 inter se clearly shows the causal correlation between the origin of supra-orbital ridges and the shifting of the orbitae, for the less this shifting, the less strong the ridges will be.

This appears even more distinctly from a comparison of Fig. 5A and Fig. 5B.

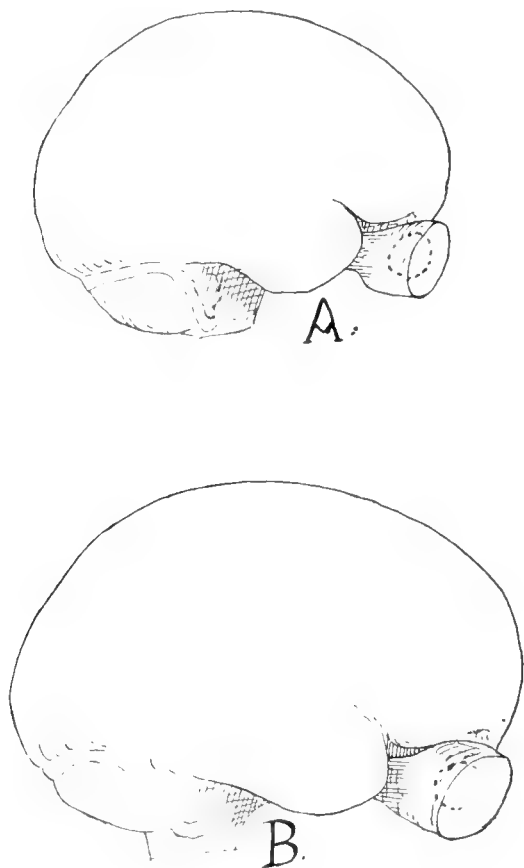
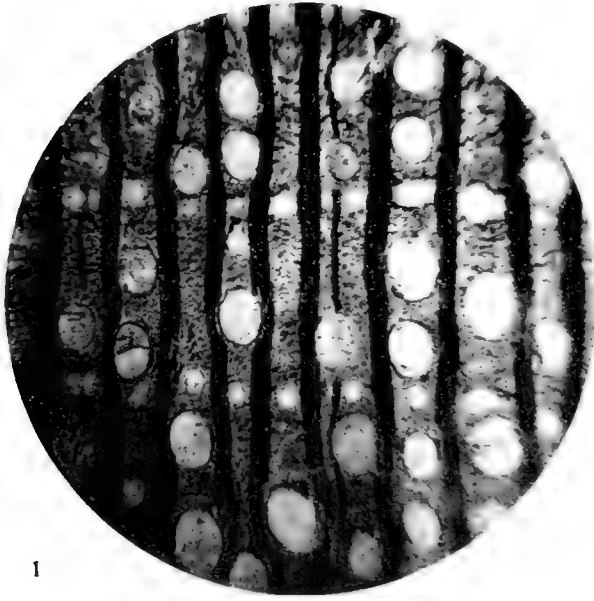


Fig. 5.

Fig. 5A shows a cast of cranial cavity and orbita of a one-month-old child, and Fig. 5B that of an adult man. It will be seen

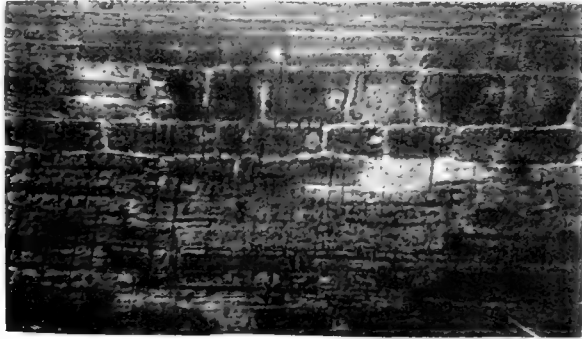
R. Kräusel: „Ueber einen fossilen Baumstamm von Bolang (Java), ein Beitrag zur Kenntniss der fossilen Flora Niederländisch-Indiens.“



1



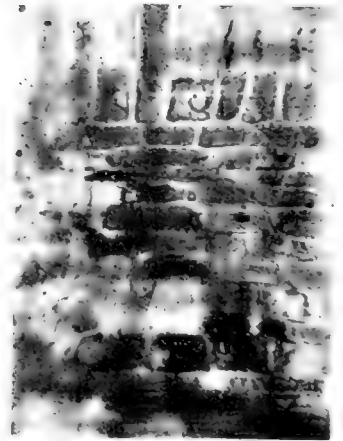
3



4



2



5

Kräusel phot.

that there is no question about a displacement of the orbita, in the baby as in the adult the orbita is situated subcerebral, which accounts for the complete absence of supra-orbital ridges in man.

The subcerebral position of the orbitae is a typical feature of the human skull, by which it is distinguished from all other mammalian skulls. In this respect the Orang skull is most like that of man. Parenthetically I call attention to my former pronouncement, quite in harmony with the fact established here: that all typical human somatic properties are persisting fetal features.

The Figures 4A and 4B also induce me to say something relative to the so-called flattening of the skull of Anthropoids. The hypothesis that the skull of Anthropoids has been flattened through mechanical causes, I consider, in principle, erroneous, as it is based only on deficient observation and inaccurate measurement. As to the latter it must be considered as a fundamental error when, in determining the length-height-index of the skull, the greatest length of the skull is considered to be the distance between two points lying on the outside of the skull. According to this method the height of the skull should be measured from the basion to the superior margin of the crista sagittalis. For a comparison of the forms of skulls of allied species measures should be used that cannot be influenced by a difference in thickness of the cranial bones, or by other adventitious circumstances. Points on the inside of the skulls should be used.

But the hypothesis that the Anthropoid skull is flattened, rests on deficient observation, as stated above. A flattening of the skull would necessarily entail a transformation of the cranial cavity. Now when comparing the relative figures it will be seen that in *Macacus* the brains of the adult individual with his large supra-orbital ridges are not flatter than those of the young individual, in which the ridges were lacking; it will furthermore be seen that the cranial cavity of the adult Orang in the frontal region is still as much vaulted as in the young specimen.

The anthropomorphous child has a frontal vault that is visible on the outside. The absence of this vaulting in the adult skull is not to be ascribed to a flattening, undergone by the frontal region, but is due to a shifting of the orbits anteriorly and to their consequent precerebral situation. From the vaulted front a new roof overlaps the orbita, and the originally apert frontal vault has thereby become an occult one.

Mathematics. — “Representation of a Bilinear Congruence of Twisted Cubics on a Bilinear Congruence of Rays.” By Prof. JAN DE VRIES.

(Communicated at the meeting of February 25, 1922).

In a communication entitled: Congruences of Twisted Cubics in connection with a Cubic Transformation (these Proceedings Vol. XI, p. 84, 1908) I have shown that the congruence of the twisted cubics ρ^3 through five points (congruence of REYE) may be converted by a simple transformation ($x_k y_k = 1, k = 1, 2, 3, 4$) into a sheaf of rays. Now I shall show how a different congruence [ρ^3] likewise by means of a cubic transformation, may be represented on a bilinear congruence of rays.

§ 1. The transformation in question arises in the following way. Three crossing straight lines a_1, a_2, a_3 are the axes of involutions of planes with pairs $a_k, a'_k (k = 1, 2, 3)$; to the point of intersection P of the planes a_1, a_2, a_3 the point of intersection P' of the corresponding planes a'_1, a'_2, a'_3 is associated.

For a point A_1 of a_1, a_1 is indefinite; any point of the straight line t_{23} which is the line of intersection of the planes a'_2, a'_3 corresponding to A_1 , may be considered as the image of A_1 . To the points of the singular straight line a_1 the rays of a quadratic scroll $(t_{23})^2$ having a_2 and a_3 as directrices are therefore associated.

Let t be a transversal of a_1, a_2 and a_3, S the point of intersection of the three planes a'_k associated to the planes $a_k \equiv ta_k$. Evidently S is associated to every point of t . The locus of the singular points S is a twisted cubic σ^3 , each point of which is represented by a ray of the quadratic scroll $(t)^2$ having a_1, a_2 and a_3 as directrices.

S being especially associated to the points A_1, A_2, A_3 where t rests on a_1, a_2, a_3, σ^3 is the partial intersection of the three scrolls $(t_{23})^2, (t_{31})^2, (t_{12})^2$; these have in pairs a straight line a_k in common.

When P describes the straight line r , the pencils (a_k) become projective; also the pencils (a'_k) become projective and they produce a twisted cubic ρ^3 which is the image of the straight line r . As r

cuts two rays of each of the scrolls $(t_k)^2$, ϱ^3 has the straight lines a_k as chords; it rests in two points on σ^3 because r meets two rays t .

Let us now consider the *bilinear congruence of rays* $[r]$ which has two of the straight lines t as directrices. Through the cubical transformation it is transformed into the congruence $[\varrho^3]$ of which the curves ϱ^3 pass through two fixed points S_1 and S_2 and have the three fixed straight lines a_1, a_2, a_3 as bisecants¹⁾.

Inversely any congruence $[\varrho^3]$ with two base points S_1, S_2 and three fixed bisecants a_k can be represented on a bilinear congruence $[r]$. With a view to this we take two transversals t_1, t_2 of the straight lines a_k and we define the involution of planes through a_k by associating the planes $(a_k S_1)$ and $(a_k S_2)$ to the planes $(a_k t_1)$ and $(a_k t_2)$.

§ 2. The curve ϱ^3 degenerates as soon as the ray r rests on one of the singular lines σ^3 or a_k .

If r passes through the point S of σ^3 its image is composed of the straight line t associated to S , and a conic ϱ^2 through S_1 and S_2 , cutting a_1, a_2 and a_3 . The locus of the conics ϱ^2 is the dimonoid of the fourth order, Δ^4 , which has threefold points in S_1 and S_2 , contains the straight lines a_k and has a double torsal straight line $S_1 S_2$.

The image of Δ^4 is the scroll $(r)^6$ with directrices ϱ^3, t_1 and t_2 , where t_1 and t_2 are threefold, which has the straight lines a_k as double generatrices. This may be verified by combining $(r)^6$ with a curve μ^3 , which is the image of a straight line m .

If the ray r is to rest on a_1 , it must belong to one of the plane pencils having the points $B'_1 \equiv a_1 t_1$ or $B''_1 \equiv a_1 t_2$ as vertex and belonging to the bilinear congruence of rays $(1, 1)$. The former plane pencil lies in the plane $B'_1 t_2$; the image of this plane is the scroll $(t_{22})^2$ combined with the plane $S_2 a_1$. For $[\varrho^3]$ there is found from this a pencil of conics which have S_2 and the intersections of a_2 and a_3 with the plane $S_2 a_1$ as base points. The fourth base point is the intersection with the straight line b'_{22} , which, as a transversal through S_1 of a_2 and a_3 , is the image of the point B'_1 . Here we have therefore a group of degenerate figures each consisting of the straight line b'_{22} and a conic of the pencil in question.

1) This congruence has for the first time been investigated by M. STUYVAERT (Dissertation inaugurale, Gand 1902). A different treatment of the "Congruence of STUYVAERT" is found in the thesis for the doctorate of J. DE VRIES, Utrecht 1917, where also the literature on bilinear congruences of twisted cubics is mentioned.

There are of course *five* more analogous groups represented by the plane pencils having their vertices in $B''_1, B'_2, B''_2, B'_3, B''_3$.

§ 3. A degeneration into three straight lines is represented by a ray of (1, 1), which cuts the singular lines twice. This is among others the case with the bisecant d of σ^3 which rests on t_1 and t_2 (and differs from a_1, a_2, a_3). Its image consists of the straight line $d_{1,2} \equiv S_1 S_2$ and the two transversals t' and t'' that rest on $d_{1,2}, a_1, a_2$ and a_3 and that are the images of the points where d rests on σ^3 .

The image of the ray $B'_1 B''_2$ consists of the line of intersection of the planes a'_1 and a'_2 corresponding to the planes $\alpha_1 \equiv a_1 B''_2$ and $\alpha_2 \equiv a_2 B'_1$ and of the straight lines $b'_{2,3}$ and $b''_{1,3}$. Through combination of the points B'_k and B''_l we find in this way *six* configurations ϱ^3 formed by three straight lines.

The straight line $b'_{2,3}$ lies on Δ^4 ; together with S_2 it defines a plane; the straight line in this plane through S_2 intersecting a_1 forms together with $b'_{2,3}$ and the straight line t resting on it a configuration ϱ^3 .

There are apparently five analogous configurations; the congruence $[\varrho^3]$ contains accordingly in all *thirteen* of those figures, each consisting of three straight lines.

§ 4. The curves of $[\varrho^3]$ resting on a straight line l , are represented by the straight lines r of the (1,1), which cut a curve λ^3 that has a_1, a_2, a_3 as chords and that meets σ^3 twice. These straight lines r form a scroll of the sixth order, $(r)^6$, with threefold directrices t_1, t_2 and double generatrices a_k . The straight line r_0 which is a chord of λ^3 , hence a double generatrix of $(r)^6$, has for image a curve ϱ_0^3 that meets l twice and which is therefore a double curve of the image of $(r)^6$. As therefore an arbitrary straight line is cut twice by only *one* ϱ^3 , $[\varrho^3]$ is a *bilinear* congruence.

The image μ^3 of a straight line m has four points on a_1 in common with $(r)^6$, for this curve cuts the double straight line a_1 in two points. Besides the straight lines a_k μ^3 and $(r)^6$ have six more points in common; hence the image of $(r)^6$ is a surface of the sixth order, A^6 , with three double lines, a_k , and the double curve ϱ_0^3 .

If μ^3 passes through a point of the line t_1 (which is threefold on $(r)^6$, m contains only three points of A^6 outside the singular lines; here S_1 and S_2 are therefore threefold points.

On A^6 there lie also the six lines b (§ 2) as component parts of the degenerate figures of which the conics ϱ^3 rest on l .

§ 5. The transformation used here, gives also the representation of *another* congruence $[\varrho^3]$. Let us consider the image of the sheaf that has M' for centre. A ray r' through M' cuts each of the scrolls (t^2) and $(t_k)^2$ twice and is therefore the image of a curve ϱ^3 through the fixed point M that cuts σ^3 and the lines a_k twice. This $[\varrho^3]$ is a special case of a congruence described by VENERONI¹⁾.

Through a point there passes *one* ϱ^3 of this congruence. A curve μ^3 , the image of a straight line m , sends *one* chord through M' ; hence m is a chord of *one* curve ϱ^3 . Also this $[\varrho^3]$ is therefore *bilinear*.

If r' intersects the curve σ^3 , ϱ^3 consists of a straight line t and a ϱ^3 through M , which intersects σ^3 twice and which rests on a_1, a_2, a_3 and t . The cone k^3 projecting σ^3 out of M' , has two points of σ^3 in common with a μ^3 ; there are accordingly seven ϱ^3 resting on m . The conics of the degenerate figures in question form therefore a surface ψ^7 ; on this a_1, a_2, a_3 are double lines (each straight line t defines *one* point S , hence one ray $M'S$, and cuts ψ^7 for this reason besides in a_k in one more point) and σ^3 is a threefold curve (t meets three generatrices of k^3).

The surface ψ^7 is represented on a plane by the chords of σ^3 ; it is therefore a rational surface and belongs to the group of homaloids to which I have drawn attention in a communication of Vol. XX, p. 419 of these Proceedings.

If r' rests on a_1 , ϱ^3 degenerates into a straight line t_{23} (the image of the point $a_1 r'$) and a ϱ^3 of the plane α corresponding to the plane $\alpha' \equiv M'a_1$. The conics ϱ^2 form a pencil with base points M , the points A_2 and A_3 of a_2 and a_3 , and the intersection of α with σ^3 , which point does not lie on a_1 . Each ϱ^3 is connected with a straight line t_{23} and this rests on a_2, a_3 and σ^3 .

There are accordingly in all *four* systems of compound figures ϱ^3 .

The chord of σ^3 passing through M' , is the image of a ϱ^3 composed of two straight lines t and the straight line through M which cuts them and which is at the same time a chord of σ^3 .

The transversal of a_1 and a_2 through M' is the image of a ϱ^3 formed by a straight line t_{23} , a straight line t_{13} and their transversal through M which rests at the same time on a_1 and a_2 .

The transversal through M' of a_1 and σ^3 is the image of a ϱ^3 formed by a straight line t , a straight line t_{23} and their transversal through M which rests at the same time on a_1 and on σ^3 .

There are therefore in all *seven* figures ϱ^3 consisting of three straight lines.

¹⁾ Rend. Palermo XVI, 209.

The curves ρ^3 resting on a straight line l , are represented by the generatrices of the cone that projects the curve λ^3 out of M' . As this cone is cut by a μ^3 in nine points, the curves ρ^3 intersected by l form a surface \mathcal{A}^9 . On this surface $\alpha_1, \alpha_2, \alpha_3$ and σ^3 are three-fold lines, because any straight line t_{kl} and any line t cuts the cone (M', λ^3) three times and the image of the double generatrix of this cone is a double curve of \mathcal{A}^9 . Any curve of $[\rho^3]$ has 8×3 points in common with \mathcal{A}^9 on the singular lines; hence M is a triple point of \mathcal{A}^9 .

Physics. — “*Research by means of Röntgen-Rays on the Structure of the Crystals of Lithium and some of its Compounds with Light Elements. II. Lithium-Hydride*”. By J. M. BIJVOET and A. KARSSSEN. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of February 25, 1922.)

1. *Introduction.* The investigation with X-rays on the structure of lithium-hydride was taken up in connection with the analogy drawn by MOERS¹⁾ between lithium hydride and the heteropolar alkali halogenides.

2. *Röntgenograms.* The photographs were made as described in our preceding paper²⁾. The difficulty presented itself that after the exposures the hydride-content had been reduced by 15 or 20 percents of weight. The parasitical lines were eliminated: by comparing the photographs of samples of decreasing hydride-content (the place of the LiH-lines appeared to be independent of the degree of decay, hence no formation of mixed crystals); by photographing a coarse crystallized, non-rotated sample, appearing the interference lines of LiH markedly distinguished by dots of greater intensity; by checking up the parasitical lines by those of LiOH).

3. *Calculation.* The table contains for LiH the values of $10^8 \sin^2 \frac{\theta}{2}$ for the centres of the α -lines. As appears from the occurrence of a factor $77,5 \pm 0,5$ LiH is regular, and the side of the elementary cell $a = 4,10 \cdot 10^{-8}$ cm. From this common factor the number of particles per elementary cell, n is calculated to be 4.30, with the aid of the density according to MOERS, mol. weight, constant of AVOGADRO, and wavelength $C_{r_{K\alpha}}$ (resp. 0,816; 7,94; $0,6062 \cdot 10^{11}$ and $2,284 \cdot 10^{-8}$). This points to $n = 4$, which is in agreement with the supposed NaCl structure together with the absence of the planes of mixed indices.

¹⁾ MOERS, Z. f. allg. u. anorg. Chem. **113**, 179, (1920).

NERNST, Z. f. Elektrochemie **26**, 323 and 493 (1920).

²⁾ BIJVOET and KARSSSEN. These Proceedings Vol. XXIII, p. 1365.

Putting $n=4$ the said common factor determines the density at $0,76 \pm 0,01^1)$. In absence of all further crystallographical data we have confined ourselves to the question whether sticking to a NaCl or ZnS structure an electron grouping could be found, according to the intensities of the reflections found.

The table gives the observed and calculated intensities. Only those factors which bring about an abrupt change in the intensity as function of Σh^2 , have been taken into account, viz. the factor of the number of planes and the structure factor, in which the influence of the configuration of the electrons too has been accounted for. For this were tested some approximative suppositions. We have considered the possibility that the valency-electron remains near its mother-nucleus (atomic lattice); that the Li has lost its valency-electron to the hydrogen (ion lattice)²⁾; that binding of Li and H takes place by means of rings of electrons revolving round the connecting line in planes normal to the non intersecting trigonal axes halfway the Li and H nuclei (binding circles; passing along a trigonal axis two-electron-rings may be imagined between Li and H: molecular lattice, case A; or one-electron-rings between Li and H as well as between H and Li, case B).

As to the orbits of the electrons it has been assumed: 1. that the electrons are so near to their nucleus that they may be supposed to lie in one point (points; reflecting power proportional to the number of electrons); 2. that the connecting line of nucleus and electron is of a definite length ϱ , and is equally occurring in all orientations throughout the part of the crystal that is cooperating in the interference (spheres; diminishing factor for such an electron

$\frac{\sin 2\pi \frac{\varrho H}{a}}{2\pi \frac{\varrho H}{a}}$, in which $H = \sqrt{\Sigma h^2}$ ³⁾); and 3. that these connecting

lines are in planes normal to the non-intersecting trigonal axes, all the directions equally occurring in those planes (rings: diminishing factor $J_0\left(2\pi \frac{\varrho H}{a} \sin \gamma\right)$, in which J_0 is the Bessilian-function of the order of magnitude 0 and γ the angle between orbit and lattice plane⁴⁾). In the binding circles also only circular orbits have been

¹⁾ Imperities have no influence on this value of the density, as there is no formation of mixed crystals.

²⁾ Also the less probable case Li-H⁺ has been considered.

³⁾ Cf. KOLMEYER, These Proc. Vol. XXIII N^o. 1, p. 120.

⁴⁾ Cf. COSTER, These Proc. Vol. XXII N^o. 6, p. 536.

considered, and here too relation of phases has been neglected (diminishing factor as under 3).¹⁾

The influence of the heat motion, of which nothing is known for the different electrons, was left out of consideration. The radius of the comparatively small inner ring of Li has always been taken equal to BOHR'S initial value²⁾; in all the suppositions mentioned it has been examined what values of the radii of the other orbits made the calculated and observed intensity concordant. Finally the supposition "rings, $q_{\text{H}^-} = \pm 5/6$ times the radius of a two-quantum ring in a free H⁻-ion" appeared to give the best agreement. As a specimen some of the calculated intensities are given i. a. those for BOHR'S initial values of q , and in the last column the case $q_{\text{H}^-} = \pm 0,6a$ and $q_{\text{Li}^+} = \pm 0,05a$, which is in agreement with the observations.

In how far the factors neglected here, as heat motion, and the occurrence of non-circular orbits, may affect the conclusions drawn here, must at present be left undecided.

4. *Summary.* The Röntgenogram of lithium hydride (method DEBYE-SCHERRER) has been taken with K_{Cr} rays. LiH appears to crystallize regularly with 4 LiH per elementary cell. [Side $a = 4.10 \cdot 10^{-8}$ cm.]. The density is found to be $0,76 \pm 0,01$. On the basis taken for the calculation the following assumptions appeared to be most satisfactory: NaCl-structure with positive Li-ions and negative H-ions; systems of two-electron rings both round Li- and H-nuclei with radii resp. $\pm 0,05a$ and $\pm 0,6a$, the planes of which are normal to non-intersecting trigonal axes.

In conclusion we express our great indebtedness to Prof. SMITS for his valuable help and the great interest he took in our work.

Laboratory of Physical and Inorganic Chemistry.

Amsterdam, February 15, 1922.

¹⁾ In COSTER'S computation of the binding circles of diamond this has also been introduced, whereas KOLKMEYER bases his calculations on an undisturbed phase relation.

²⁾ BOHR, Phil. Mag. (VI) 26 490 (1913).

Bacteriology. — “*Studies about D’HERELLE’S Bacteriophagus*”. By J. W. JANZEN and L. K. WOLFF. (Communicated by Prof. C. EYKMAN).

(Communicated at the meeting of February 25, 1922).

I. *The Bacteriophagus in Enteric Fever.*

We have succeeded in proving the existence of this bacteriophagus in the faeces of patients recovering from enteric fever, as has also been described by D’HERELLE.

If D’HERELLE’S views are right, it must be possible to influence the process of enteric fever favourably by administering bacteriophagum antityphoideum.

We have tried this in three cases and perhaps we have observed a somewhat favourable result, but not a striking success. The explanation hereof might be found in the fact that this bacteriophagus did not happen to be adjusted at the bacterium, that caused the illness of these patients. We have considered it worth while to examine this systematically.

We have been able to make use of three bacteriophagus specimen, two of which were from the faeces of patients recovering from enteric fever, the third from the faeces of a healthy person who had had enteric fever forty years ago. We have examined the effect of the bacteriophagi as opposed to 17 typhoid strains, 15 of which came from the collection of the Laboratory for Hygiene, the two others from the blood of patients out of which the bacteriophagus had also been taken. We have steadily examined the clearing up of the broth, which has turned slightly turbid by typhoid bacilli 6 hours old from agarcultures, the checking of the growth of typhus-bacilli in broth, and finally the formation of little islands on the agarplate(plages).

What can be the cause of this difference in behaviour?

It might be supposed that the uninfluenced typhoid strains would be so called resistant strains.

This would be possible for some strains that are not influenced by any of the three bacteriophagus strains (3, 8, 20).

But we also see that the bacteriumstrain which is influenced by one bacteriophagus is not influenced by the other, and vice versa.

TABLE.

1. Clearing up of the typhoid bacilli distributed in the broth.
2. Checking of the growth of typhoidbacilli.
3. Formation of little islands on the agarplate, on which some of the contents out of tube I has been smeared.

| typhoidstrain | Bacteriophagus Wi. | | | Bacteriophagus Sm. | | | Bacteriophagus Re. | | |
|---------------|--------------------|------|------|--------------------|------|------|--------------------|------|------|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Sm. | ± | ++++ | ++++ | ++++ | ++++ | ++++ | - | + | ++++ |
| Wi. | ++++ | ++++ | ++++ | ± | - | - | - | - | - |
| 1 | - | - | - | - | +++ | ++++ | - | +++ | ++++ |
| 3 | - | - | - | - | - | - | - | - | - |
| 8 | - | - | - | - | - | - | - | - | - |
| 9 | ++++ | ++++ | ++++ | - | +++ | ++++ | ± | ++ | ++++ |
| 15 | - | ± | ++++ | - | - | ++++ | - | ++ | ++++ |
| 19 | - | ± | ++++ | - | - | ++++ | - | - | ++++ |
| 20 | - | - | - | - | - | - | - | - | - |
| 23 | ++++ | ++++ | ++++ | - | +++ | ++++ | - | - | - |
| 24 | - | ++ | ++++ | - | - | - | - | - | - |
| 25 | ++++ | ++++ | ++++ | - | +++ | ++ | - | +++ | ++++ |
| 26 | ++++ | ++++ | ++++ | ++ | +++ | ++++ | ++ | ++++ | ++++ |
| 27 | - | ± | ++++ | - | - | - | - | - | - |
| 29 | - | ++++ | ++++ | - | - | - | - | - | - |
| 31 | - | ± | ++++ | ± | ++ | ++++ | - | ++++ | ++++ |
| 32 | +++ | ++++ | ++++ | - | +++ | ++++ | - | ++ | ++++ |

Bacteriophagus Wi negative with regard to 1, 3, 8, 20

„ Sm „ „ „ „ „ Wi, 3, 8, 20, 27, 29

„ Re „ „ „ „ „ Wi, 3, 8, 20, 23, 24, 27, 29.

Bij agglutination with a highly agglutinating horseserum (Saxonian serum-works) no difference between the strains could be demonstrated, they all agglutinated to $1/40000$.

So it will be necessary to find or to prepare a bacteriophagus which also affects the negative strains.

For the time being we have not succeeded in vitro to adapt the bacteriophagus to these. So we shall have to wait until a new

bacteriophagus is found which fills up this gap, if need be we can then administer a mixture of the various bacteriophagi.

We have been able to convince ourselves that, with a dose of 10 cM. bacteriophagus per os, the bacteriophagus was already to be found the next day in the faeces of two typhoid patients who had not had it before.

D'HERELLE has proved that the bacteriophagus is not absorbed by foreign bacilli on which it has no effect.

Our bacteriophagus however was absorbed by living typhusbacilli who were not influenced in their growth by our bacteriophagus.

February 1922.

*Amsterdam, Lab. for Hygiene of the
University.*

Bio-Chemistry. — “*Experiments on Anaphylaxis with Azoproteins*”.

By K. LANDSTEINER. (Communicated by Prof. C. H. H. SPRONCK.)

(Communicated at the meeting of January 28, 1922).

In previous articles the writer described methods for producing immune sera, acting upon known chemical groups. These methods are based upon the use of antigens, consisting of proteins, which are chemically combined with substances of simple constitution.¹⁾

As already indicated, the question suggests itself as to whether anaphylaxis can be produced by these compounds and what is the action in anaphylaxis (sensitization and shock) and antianaphylaxis of each of the two components of the antigen, viz. the proteins and the simple substances combined with it. The significance of these problems for the theories of immunity and anaphylaxis and the knowledge of the condition of hypersensibility produced by simple substances is evident (cf. DOERR²⁾).

The experiments presented here³⁾ form part of a series, the carrying out of which has been delayed because of external circumstances.

The guinea pigs were sensitized by means of azoprotein⁴⁾ prepared from horse serum and p-arsanilic acid (1 gr. of atoxyl for 100 cc. of serum).

For the second injection an azoprotein formed by combining fowl serum and p-arsanilic acid was employed. The use of a number of other azoproteins was rendered difficult because of their toxicity when injected intravenously.

Results: It was found to be more difficult to produce the anaphylactic state with the substances mentioned above than with the proteins usually employed, and in the experiments to be described it was necessary to make three intraperitoneal injections, corresponding to 0.5 to 1.0 cc. of serum each, in order to produce considerable effects.

1) Zeitschr. f. Immun. 26, p. 258 (1917), Biochem. Zeitschr. 86, p. 343 (1918).

2) DOERR, Schweiz, med. Wochenschr. 1921. No. 41.

3) Details will be given later.

4) l. c. Bioch. Zeitschr. 86, p. 359.

In the case of 14 of the sensitized guinea pigs, the reinjection was made intravenously, using 1 to 2 cc. of azoprotein¹⁾ per 500 gram weight of the animals. 5 animals died within a few minutes, 3 showed severe, 5 slight manifestations of anaphylactic shock. Nine control animals showed no symptoms.

Five animals treated in the manner described showed no anaphylactic reaction after the intravenous injection of azo-compounds obtained by combination of tyrosin and p-arsanilic acid; the injection of azoprotein (fowl serum + p-arsanilic acid) made an hour later failed to produce shock. As a control experiment, in 3 animals an azo-compound of metanilic acid and tyrosin was used for the intravenous injection. These animals showed anaphylactic symptoms on the subsequent injection of azoprotein (fowl serum + p-arsanilic acid).

The results obtained demonstrate that guinea pigs previously injected with an azoprotein (horse serum + arsanic acid), show anaphylactic reactions upon being reinjected with another azoprotein containing the same group, i.e. fowl serum + arsanic acid; but they do not show such symptoms upon being reinjected with a compound of arsanic acid and a substance of simple composition, i.e. tyrosin. The latter substance, on the other hand, seems capable of desensitizing the animals.

The Hague.

Laboratory of the "R. K. Ziekenhuis".

¹⁾ Prepared as indicated in *Biochem. Zeitschr.* **86**, p. 362.

Physiology. — “*On the Causes of the Emigration of Leukocytes*”¹⁾

By K. J. FERINGA. (Communicated by Prof. H. J. HAMBURGER.)

(Communicated at the meeting of February 25, 1922).

DE HAAN²⁾ has suggested a method by which in a simple manner, without injuring the laboratory animal, large quantities of polynuclear leukocytes can repeatedly be obtained. He injected into the abdomen of his animals fluids such as a starch-solution in NaCl 0.9, and other harmless fluids and thereby obtained invariably a homogeneous emigration of polynuclear leukocytes.

My own investigations were performed systematically according to this method, with a number of liquids in order to demonstrate a definite chemical cause for the emigration of the leukocytes. I experimented on rabbits.

For shortness sake I will only summarize the results of these experiments.

Whatever liquids were injected (electrolytes, non-electrolytes, more or less physiological fluids such as RINGER's solution, ultra filtrate of serum, sterile serum, olive-oil or paraffin) the result was invariably an exudation with emigration of many leukocytes. The process of this emigration was the same in all cases. *From this I concluded that the emigration is not brought on by a specifically chemotactic influence exercised by definite substances upon the leukocytes.*

However, there was still a factor that had been left out of consideration, viz. the *concentration of the hydrogen-ions*, which recent inquiries have proved to play a prominent part in different manifestations of life.

I considered it rather interesting to ascertain the proceeding of the H-ion concentration in the injected liquid at various intervals after the injection.

We used for this purpose the *colorimetric method* and applied *phenol-red* and *cresol-red*, recommended by CLARK and LUBS³⁾.

Determinations were made in serum of venous blood and in normal

¹⁾ A more detailed communication will appear elsewhere.

²⁾ J. DE HAAN, i.a. Thesis. Groningen 1920.

³⁾ CLARK and LUBS, Journ. of bact., 2. 1. 109, 191 (1917).

abdominal transudate; the pH of serum was slightly less than 7,6 and that of normal abdominal transudate 7,6.

When fluids were injected into the abdominal cavity, a pH of 7,2 invariably occurred in the exudation after a short time ($\pm \frac{1}{4}$ hour), no matter whether the injected fluid was acid or alkaline beforehand. This was the same for all injected substances, also for strongly buffered fluids, such as serum. Only the interval before a pH of 7,2 is reached, is somewhat longer. This also applied to oil and paraffin-injections, the centrifugalized fluid then presented a pH of 7,2.

It appears, then, that *a difference of pH from 0,3 to 0,4 exists between the blood and the exudation*. At the same time it appeared that emigration of polynuclear leukocytes results from the injection of the same fluids.

There is now every reason for correlating the constant occurrence of emigration with this constant phenomenon of the changed pH, which also always manifests itself, however different the injected fluids may be.

The question may be asked: in how far this differing H-ion concentration may be answerable for the emigration. I have endeavoured to solve this problem by maintaining artificially in the injected fluid a pH of 7,6 or a little higher, through the addition of alkali, and comparing the result obtained with a control-animal, in which the injected fluid was left to itself. I found from three such experiments that in the first case no emigration of polynuclear leukocytes ensued, which, however, revealed itself with the control-animal.

It is evident from these experiments that *the degree of acidity is, indeed, the causative factor of the emigration of the polynuclear leukocytes*; it being the only factor which has altered in the experiments mentioned.

We now have to go into the question in what manner this established difference in H-ion concentration with the blood can bring about the emigration. Presumable potential differences between fluids with various H-ion concentration are the first to suggest themselves; such potential difference might well effect a movement of cells in one direction, in casu an emigration. I am analogously reminded here of the well-known *cataphoretic phenomena* found i.a. by HÖBER and his pupils especially in red blood-corpuseles.

I thought it desirable by following the example of HÖBER to perform cataphoretic experiments with red blood-corpuseles, with polynuclear leukocytes and with mononuclear leukocytes of the rabbit in order to ascertain whether they behaved differently towards

the galvanic current. This appeared, not to be the case: all of them moved towards the anode, their charge was consequently negative. Through the addition of acid we managed to change their charges: when the pH was made less than 4.8, they moved towards the cathode.

In the body, where pH is always greater than 4.8, they will always be moved by the current towards the anode. This, then, does not afford an explanation of the various behaviour of the different kinds of blood-corpuseles in the case of exudation. However, we need not, on that account, exclude the possibility of the exudation of the polynuclear leukocytes being caused by a potential difference, as besides a potential difference other factors come into play, which may cause or prevent emigration, i.e. the surface-properties with regard to the capillary wall, and the ameboid mobility. Hence the passive cataphoresis becomes complicated on account of these surface-actions. These actions will vary the effect of the cataphoresis in different cells in accordance with their composition; even in the absence of emigration, the cataphoretic effect even on red blood-corpuseles will reveal itself in the considerable accumulation of blood-elements in the abdominal vessels.

Now I have tried to demonstrate potential differences between two fluids differing only in the H-ion concentration. To this end we made use of a so-called "ölkette". I succeeded in demonstrating with *benzaldehyd* and *benzylalcohol* as *oilphase*, potential differences between fluids with a pH of 7.2 and 7.6. When adding lecithin or a mixture of lecithin and cholesterol to the oilphase, the potential difference was considerably greater. An addition of cholesterol alone, however caused the potential difference to disappear altogether.

These experiments have proved it to be very probable, that *through the difference in pH there is also a difference in potential* between the circulating blood and the exudation. Preliminary experiments justified the same conclusion.

With non-polarisable electrodes we found that under normal conditions the blood is positive (however slightly) relative to the abdomen, while after the injection of a fluid into the abdomen, a reverse potential difference manifests itself. These experiments, however, will have to be prosecuted further.

Since we have seen that the bloodcorpuseles may be moved by electromotive forces, we are justified in assuming that under the influence of the difference in acidity between the blood and the exudation, which causes a potential difference, the polynuclear leukocytes are moved towards the exudation. The anomalous be-

haviour of the lymphocytes and especially the red blood-corpuscles, may, as stated above, be ascribed to other surface properties of these cells.

In conclusion we may state, therefore, that through injection of any fluid whatever, an increased prolonged acidity can be demonstrated at the place of injection, which may reasonably be assumed to give a certain direction to the ameboid movements of the leukocytes, which reveals itself in the constant occurrence of the emigration of the polynuclear leukocytes.

I may still add that in no case does the increased acidity exist longer than 18 hours, after the injection of aqueous fluids, but that it persists longer after oil injections; this is the reason why with oil the emigration lasts longer, as is borne out by all phenomena, i.e. the changes in the blood-formula, which cannot be gone into any further here. Neither can I expatiate here on the cause to which the increased acid formation itself is due. I can state only that there is no excessive accumulation of carbonic acid. The only factor we can take into consideration is a diminution of the normal reserve of alkali under the influence of the formation of acids other than carbonic acid.

Now it is of vital importance to know whether our conclusions regarding the emigration of leukocytes in sterile abscesses and exudations, also apply in general to every migration of leukocytes through the body, e.g. to the emigration of leukocytes in exudations of bacterial origin and to the emigration (normal and pathological) of the white bloodcorpuscles from the bone-marrow in the blood-circulation. Concerning the latter we are inclined to believe that normal supply of the polynuclear cells in the blood from the bone-marrow is also procured under the influence of a potential difference between bone-marrow and blood. It may also be possible that, when that supply from the bone-marrow proceeds abnormally, as in cases of *leukæmia*, the relation between the pH in the blood and the bone-marrow is altered. It also avails to know the reason why, in the case of fatal infections, the bone-marrow does not react on the stimulus of inflammation, why no leukocytes are transmitted to the nidus of the inflammation.

It may be also that without a potential difference between bone-marrow and blood or between blood and the nidus of inflammation, the emigration of leukocytes is impossible. It should at the same time be noted, whether the distribution of lecithin and cholesterol in the body may have influence on the generation of electric currents;

the significance of a proper relation of these substances for various functions of the body, has latterly been pointed out by several authors¹⁾. Furthermore we have also seen, that cholesterol, added to an intermediate phase between two fluids with different H-ion concentration, brought about an isolation which prevented an electric current. Such an insulator might, therefore, likewise prevent the occurrence of an electric current in the body.

Thus far I have been able to ascertain whether acidity plays a rôle only with regard to the abscesses in acute inflammation processes. In analogy to what we have seen in the sterile exudations, it may be expected that in pus or exudations of inflammatory nature, in which polynuclear leukocytes predominate, there will be a pH considerably smaller than that of the circulating blood. If only mononuclear leukocytes occur in the exudations or in the pus, the pH will differ little or not at all from that of the blood or the blood serum. It may be presumed, therefore, that in acute suppuration-processes there is in the pus a much lower pH than that in the serum. In chronic cases of suppuration, especially when there are no polynuclear leukocytes, the difference in pH with the blood must be much smaller. Likewise in tuberculous pus, where only mononuclear leukocytes occur, we cannot expect a great difference in pH with the bloodserum.

The pH of human bloodserum was determined again by the colorimetric method. Here we met with great obstacles in the yellow colour, which is most often peculiar to serum and in the occasional excess of fat. In accordance with the values established by EVANS²⁾ with indicators, we found also in the human serum a pH of ± 7.6 .

Pus from an acute pleuraempyema was examined. The liquid centrifugalized from the pus, had a pH of 6.9. The ill-smelling pus contained many streptococci and beyond mononuclear- many polynuclear leukocytes and remains of them.

Pus from a chronic molar abscess with acute exacerbation had a pH of 7, beyond mononuclear leukocytes also many polynuclear leukocytes and remains of them occurred in the pus.

In a case of streptococci-meningites the cerebrospinal fluid had a pH of 7.3 and contained rather many leukocytes, of which 60% were mononuclear and 40% polynuclear. The next day another puncture was made, and the fluid derived from it, proved to be much more cloudy; the pH was then rather more than 7.2. The relative number of the various kinds of leucocytes had changed now, the mononuclear cells fetching only 5% and the polynuclear as much as 95%.

It appears, then, that in these investigations the pH found, agrees with the presence of polynuclear leukocytes in the pus or in the exudation.

S U M M A R Y.

1. To bring about *the emigration of leukocytes from the blood-*

¹⁾ Cf. c.a. BRINKMAN and VAN DAM, Studien zur Biochemie des Phosphatide und Sterine 1-3. Biochem. Zeitschr. bnd. 108, H. 1/3 1920.

²⁾ C. LOVATT EVANS, The Journ. of Physiol. 54, p. 167 and 353.

circulation, chemotactic properties of definite substances do not come into play. The process of the emigration is the same, whatever may be the nature of the substances injected for the purpose of obtaining the exudation in the abdominal cavity. Neither can any special significance be attached to *fat and lipoids*.

2. As for the chemical composition of the obtained exudation, it appeared that in a short time it becomes about the same as that of the normal tissue-fluid.

3. *The injected fluid very soon reaches a higher degree of acidity relative to the blood and the normal tissue fluid*; independent of its being acid or alkaline when injected, a concentration of hydrogen ions of about pH 7,2 is produced, while the normal reaction of blood and tissue-fluid is 7,6.

4. *This higher acidity must be considered to be answerable for the emigration, since the emigration stays away, when the acid reaction is checked.*

5. In keeping with this fact also in inflammatory-abscesses, the reaction of the fluid relative to the blood is distinctly more acid.

6. It is possible *to consider the emigration as resulting from the potential difference arising under the influence of the difference in concentration of H-ions between the blood and the injected fluid, in the sense of a cataphoretic action.*

7. We call attention to the possibility, that also in other abnormal accumulations of leukocytes in the body, as in leukæmia, corresponding factors play a part.

February 23, 1922.

*From the Physiological Laboratory of the
Groningen State-Univ.*

Geology. — "*Observations on the Incandescent Sand Flow of the Valley of ten thousand smokes.*" By ROBERT F. GRIGGS. (Columbus, Ohio, U.S.A.)

(Communicated at the meeting of April 29, 1922).

Of the work done by the last expedition (1919) Dr. ESCHER has seen only the popular account in the National Geographic Magazine, September, 1921, Vol. 40 pp. 219—292. This account, written for the 725,000 members of the National Geographic Society, was manifestly not the proper place for a technical presentation of the detailed data which the geologist requires as the basis for his conclusions.

A more technical, though only preliminary, account giving more geological information has been published by Dr. C. N. FENNER, Petrologist of the cooperating party sent with the expedition by the Geophysical Laboratory of the Carnegie Institution, in the Journal of Geology, Vol. 28, pp. 569—606, 1920, under the title "The Katmai Region, Alaska, and the Great Eruption of 1912."

A further contribution by E. T. ALLEN, Chemist of the Geophysical party, dealing not directly with the Incandescent Sand Flow but with the "Chemical Aspects of Volcanism", appeared in the Journal of the Franklin Institute, Vol. 193, pp. 29—80, January, 1922.

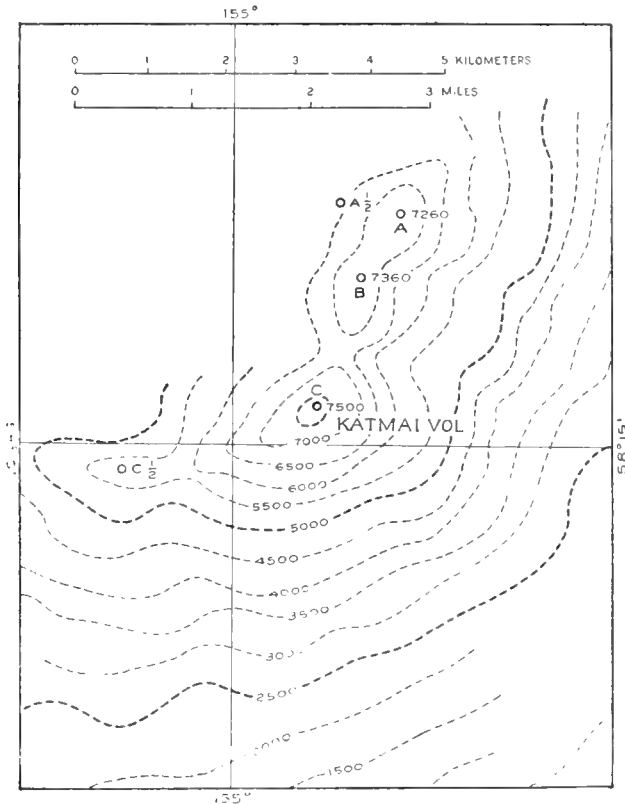
Further papers giving the scientific results of the Katmai expeditions in more detail are soon to appear in the projected Memoirs of the National Geographic Society.

Dr. ESCHER believes that the hot sand flow was made possible by the water of a crater lake which "must have" occupied the top of the mountain prior to the Eruption of 1912. He is in fact so sure of such a lake that he even figures it on his diagram.

The first and most obvious fact which renders this explanation impossible is that Katmai possessed no crater lake prior to the eruption. On page 43 is reproduced a section of the United States Coast and Geodetic Survey Chart N°. 8555 showing the condition of Katmai before the great eruption. It was a three-peaked mass without any large crater, essentially similar to its near neighbor Mageik, see map on page 45 also a photograph reproduced in the National Geographic Magazine, Vol. 31, p. 30, 1917. Both were rounded domes built up by repeated flows of viscous lava without admixture of cinders or other fragmental products such as appear in the typical composite cone.

Up till the last eruption the ejecta had consisted entirely of basic-andesite which had poured out without any explosive accompaniments of a major sort. Between the last of these flows and the

Katmai volcano before the eruption



This map shows that there could have been no crater lake before the eruption. The site of the present crater (cf. map on page 45) was occupied by three peaks whose position and altitude were determined with precision by the United States Coast and Geodetic Survey, from whose Chart N^o. 8555 the figure is traced.

recent outburst had intervened a pause probably many centuries in duration and when activity was resumed it differed materially from what had preceded. The Eruption of 1912 consisted entirely of fragmental products rather than molten lava. First came the great outpour of ash and pumice which is the subject of this note. Then Mt. Katmai blew up in a series of extremely violent explosions which left behind the present gigantic crater in place of the former mountain summit. The total quantity of rock that disappeared from

the top of Katmai during the eruption is estimated at $11,000 \times 10^6$ cubic yards (8400×10^6 cubic meters).

Associated with the change in the character of the activity was an equally great change in the composition of the magma concerned. The old lavas are dark-colored basic-andesites with a silica content of about 60 per cent.

But the new magma is a white, acid rhyolite with 75 per cent of silica.

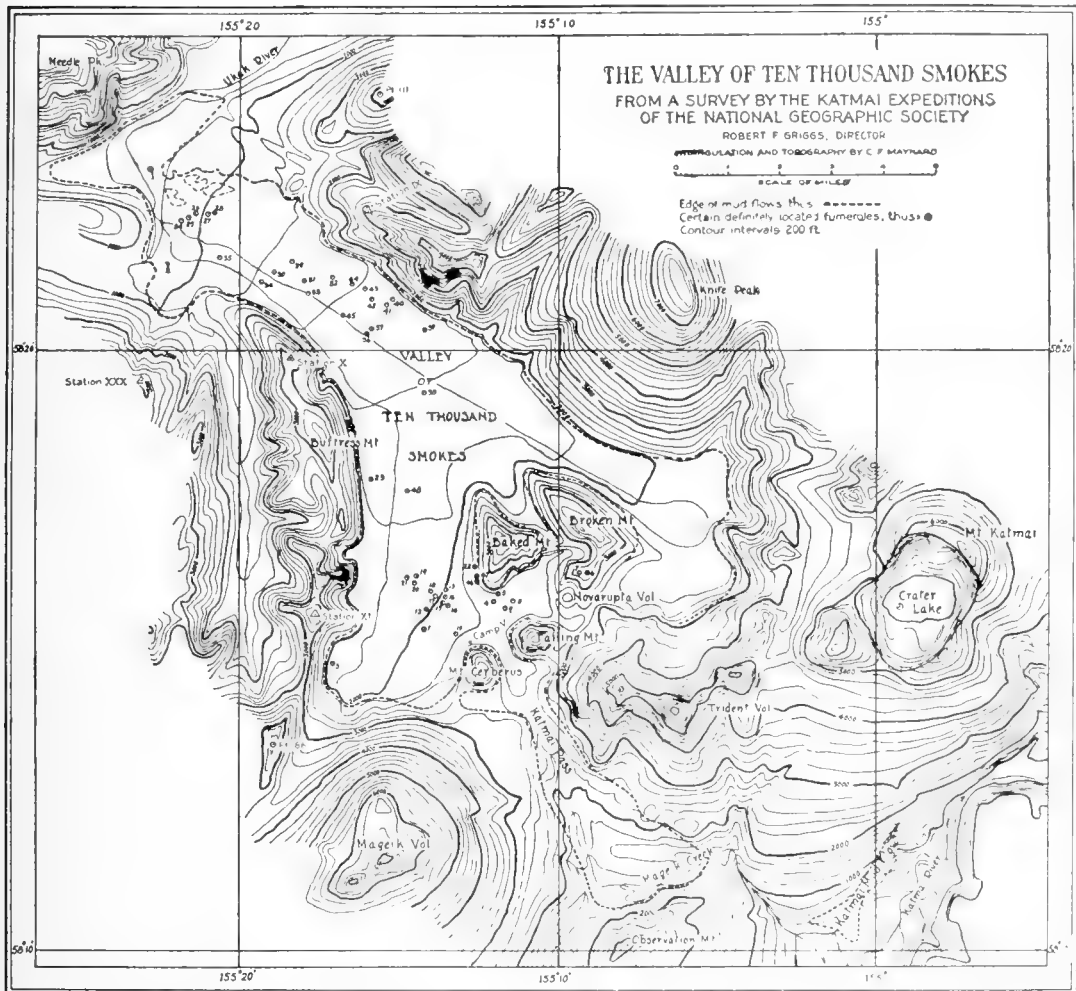
This change in composition of the magma, while without any particular bearing on the point at issue here, is of great significance in interpreting other aspects of the eruption, for it enables us to gain considerable insight into the processes operation before and during the explosions.

A second line of proof that the Incandescent Sand Flow could not have been of the type supposed by Dr. ESCHER is that the slopes of Katmai show no evidence of such a flow having passed over them. As Dr. ESCHER rightly asserts, a lahar erodes in the upper steep portion of its course. Erosion would have been particularly marked if such a flow had passed down the slopes of Katmai, since they were covered with ice, which would have melted away with great rapidity before a hot lahar. Yet the slopes down which Dr. ESCHER assumes the lahar to have coursed are still clothed by the glaciers which originally covered them. To be sure, the heads of these glaciers were blown away in the explosions of the summit of the mountain and their toes were melted back by the flow of incandescent sand across them from Novarupta down the Valley. But these accidents to the extremities only serve to emphasize the undisturbed condition of the middle slopes down which the hypothetical lahar is supposed to have run.

Instead of having flowed down the slopes of Katmai, the mass clearly moved transversely across the base of the volcano. The high sand mark, i.e. the edge of the flow, slopes steadily from south to north across the foot of Katmai. Its altitude at the south edge of the glaciers is several hundred feet greater than at the north edge, thus indicating that it flowed north along the foot of Katmai rather than westward from its heights.

A third circumstance which makes it impossible to assign the origin of the flow to Katmai volcano is the distribution of its material. A more detailed contour map than that published with Dr. ESCHER's argument (see page 45) makes it clear that the greater part of any fluid poured down the western slopes of Katmai would pass through the East arm of the Valley of Ten Thousand Smokes between Knief

Peak and Broken Mountain. A small portion might pass over the divide at Novarupta and run down between Falling Mountain and Baked Mountain. But as a matter of fact the quantity of flow material



Mt. Katmai and the Valley of Ten Thousand Smokes since the eruption. Compare Mt. Katmai with the map on page 43. The contours show that it would be impossible for a liquid flowing under gravity from top of Katmai volcano to reach the head of Mageik Creek via Katmai Pass.

in the Valley leading away from the base of Katmai appears markedly less than that in the main arm of the Valley of Ten Thousand Smokes ten kilometers across the mountains from Katmai. No liquid starting from the summit of Katmai and seeking its level under gravity could possibly reach the summit of Katmai Pass.

It is believed that the map on this page demonstrates this point

sufficiently. But it may be added that the relatively small scale map with contours no closer than 200 feet (60 meters) is much less convincing than an examination of the ground itself. I venture to assert that no one who had made field observations would have suggested the possibility of a flow from Katmai taking the course outlined by Dr. ESCHER. The arrows on his map would make out that a part of the flow turned out of the direct course and climbed the 150 meter slope between Falling Mountain and Trident, instead of continuing in a straight line down the Valley. Not only gravity but also inertia acting as centrifugal force, would have opposed any such course. The presence of the flow in the saddle of Katmai Pass and down the slopes on both sides constitutes inescapable proof that part of it originated near the divide. A good-sized crater which may have been one of the points of origin lies in fact near the summit of the pass.

Any one of these three lines of evidence alone would negative the possibility of our flow being a lahar of the Klut type. Taken together they put such a hypothesis entirely out of the question.

But, if the evidence definitely shows that our flow is not analogous with the hot lahars of Klut, the determination of its real nature is quite another question.

In our earlier studies, recognizing the evident resemblance of the terrane to an ordinary mud flow, we sought to interpret it without assigning a very high temperature to its material — hence the descriptive name applied, “hot mud flow”. It was recognized from the first, however, that no ordinary aqueous suspension could ever convert a whole forest into charcoal. Further study made it more and more clear that the mass must originally have been very hot. Charred wood occurs only near the foot of the flow, fifteen kilometers or more from Novarupts. Throughout the main part of the Valley the vegetation was entirely consumed and its ashes dissipated. The rock of a whole mountain, named “Baked Mountain”, was changed from gray-green to brick red — as though subjected to a high temperature for a prolonged period.

The stiffened tuff left behind after the sand flow had come to rest differs materially in several respects from the deposits of Klut. In the first place it was much more viscous while in action. The average thickness of the Klut lahar is estimated as only 50 centimeters. The pictures of destruction in Blitar all show a relatively thin veneer of volcanic debris covering the ground. This terminal portion moreover was not very hot as is evidenced by numerous plants with unwithered leaves standing close to the volcanic debris,

e.g. a patch of rank herbage beside the railway station at Blitar. (See this pag.)

In our flow, on the other hand, the average thickness is fifty



Photo from HELMIG & Company.

Volcanic debris from the Lahar of Klut at Blitar about 5 km. above the terminus of the flow. The unburned buildings and unwithered herbage show that the lahar could not have been very hot at this point.

times as great, indicating an entirely different sort of fluid. It is doubtful indeed if the *minimum* thickness of our flow was as low as the average thickness at Klut. Few, if any of the deposits left on the ground are less than a meter thick. Clear out to the very tip it retained an excessively high temperature. For a considerable distance beyond the present end of the flow material one finds stumps of bushes burned off by the heated material that once covered them but has been eroded away. Outside the limits of the flow itself moreover all trees were killed for some distance and grass fires were started well down toward the tip. See pages 48 and 49.

The deposits left behind, while different from the lahar of Klut, resemble closely those of the "incandescent avalanches" of Pelée and La Soufrière as described by a number of observers, e.g. ANDERSON and FLETT ¹⁾.

This similarity together with the increasing evidence of a high temperature brought out by further study has convinced us as detailed by FENNER ²⁾ that the tuff filling the Valley of Ten Thousand Smokes originated as an outpour of red-hot material very much like the incandescent avalanches that rolled down the slopes of Pelée and La Soufrière in 1902.

The differences between these and the hot sand flow with which we are dealing appear in fact to be due to differences in the cir-

¹⁾ Phil. Trans. Royal Society, A vol. 200; p. 492 et seq. 506 et seq.

²⁾ O. p. cit. p. 577.

circumstances of extrusion rather than in the character of the ejecta. Whereas the incandescent avalanches of the West Indian volcanoes issued from old vents of the central type, observations such as have been detailed in the case of Katmai exclude as possible source all of the five old volcanoes adjacent to the Valley of Ten Thousand Smokes.

A section of the sand flow close to the terminus.



Photo by L. G. FOLSOM.

The tree, about 30 cm. in diameter, was entirely reduced to charcoal. The material was much less fluid than the lahar of Klut, for it did not run out into a thin sheet as there, but remained relatively massive close to the extremity. (The sand is covered by stratified ash from Katmai and by outwash of the stream which later cut the section).

The configuration and practically continuous course of the high sand mark entirely around the Valley basin seem to leave no escape

The edge of the incandescent sand flow of the Valley of Ten Thousand Smokes.



Photo by P. H. HAGELBARGER.

The picture was taken about the same distance, circa 5 km. above the terminus, as the one of Klut. Contrast the total destruction here with the uninjured trees at Blitar. On the original surface where revealed by erosion may be seen the stumps of trees burned off just above the ground.

from the conclusion that the material originated within the confines of the Valley itself, that the vents from which it issued were located within the limits of the high sand mark. Since vents in this situation would be choked by their own products unless vigorously explosive¹ we need not be surprised if the points of issue are not certainly identifiable.

The distribution of the flow, sloping as it does both ways across two divides, shows that it could not have come from any single vent. A number of considerations suggest that many vents, rather than a few, were probably concerned. The character and distribution of the present fumaroles in the Valley, together with some other circumstances, likewise make it appear more probable that the orifices were fundamentally fissures, not centralized vents on the model of the ordinary volcano.

The nature of the vents from which the incandescent material

¹) Since the type of material composing the tuff is strictly confined to the Valley basin, not a particle of it being found on the adjacent mountain slopes, it is clear that the magma must have issued comparatively quietly, albeit the material is now thoroughly fragmented, indicating a degree of inflation comparable with the magma of Katmai which exploded with great violence.

issued may, however, remain largely a matter of opinion, but their location within the Valley is, it is believed, definitely established.

In conclusion, may I express my appreciation of the helpful spirit in which Dr. ESCHER has attempted to assist in the solution of what is admittedly a very perplexing question? I shall hope, moreover, that the necessity which I have been under of showing that his thesis does not accord with the facts will not discourage further discussion of the remarkable phenomena of the Eruption of Katmai. For it is my belief that here is presented a unique opportunity to gain an understanding of the phenomena of volcanism; that there are problems here which, in their ultimate solution, will require the coöperation of many minds approaching them from many different angles.

ERRATUM.

In Prof. PEKELHARING'S communication: "*On the Movement of Pepsine, a. s. o.*" (Proceedings Vol. XXIV, p. 269) to read p. 272, 2nd line from the top **1 mgr.** instead of 0,1 mgr.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XXV

N^{os}. 3 and 4.

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Secretary: Prof. L. BOLK.

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Mathematics. — “*Axes of Rotation of Quadratic Surfaces through 4 Given Points*”. By H. J. VAN VEEN. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of March 25, 1922).

§ 1. If we assume three points in space, any straight line l may be considered as the axis of rotation of a quadratic surface of revolution through these points. For the circles which the three points describe during the revolution round l , cut a plane through l in six points. These lie apparently on a conic k^2 which has l as axis of symmetry. Revolution of k^2 round l gives a quadratic surface of revolution (in what follows to be indicated by O^2), which has l as axis of rotation (briefly axis) and which passes through the 3 given points.

As a rule an O^2 is defined by its axis and three points; if, however, during the revolution round l two (or three) of the given points describe the same circle, there exists a pencil (net) of O^2 's that have l for axis and pass through the 3 points.

An O^2 is always defined by 3 circles with the same axis, provided these circles do not all lie in the same plane.

§ 2. The axes of the O^2 's through 4 given points $A_i (i = 1 \dots 4)$ form a complex of rays Γ , which will be investigated in what follows. By O^2 we shall understand a quadratic surface touching the sphere-circle γ^2 twice; the line p joining the points of contact, will be called *chord of contact*; the conjugated polar line of p — defined as the locus of the points the polar planes of which pass through p — is the *axis of O^2* . As a rule this locus is a straight line p' passing through the pole P of p relative to γ^2 ; if p' is indefinite only the straight line (or lines) *conjugated to p and passing through P* will be considered as axis.

As special quadratic surfaces which according to the aforesaid must be considered as O^2 , I mention: a *parabolical cylinder with a plane pencil of axes in the plane $V\infty$ at infinity* and a *pair of parallel planes with a sheaf of // axes*.

§ 3. Assume an arbitrary plane π and in it a point P . If Q is the point at infinity of a straight line of the plane pencil (P, π) , PQ can only be the axis of an O^2 touching γ^2 in its points of intersection with the polar line q of Q relative to γ^2 , but at the same time the polar plane of P relative to the same O^2 , must pass through q .

The O^2 's through A_i touching γ^2 at its points of intersection with q , form a pencil; if Q moves along the straight line at infinity r of π , q revolves round the pole R of r relative to γ^2 . We get in this way ∞^3 O^2 's cutting V_∞ in a system of ∞^3 conics k^2 touching γ^2 at its intersections with a ray of the plane pencil round R .

Now I represent the space of the conics of V_∞ on a five dimensional point-space R_5 by considering the coefficients of the equation of a k^2 as the homogeneous coordinates of a point in R_5 ; to a conic k^2 and to a linear system of ∞^k conics $(k^2)_k$ of V_∞ there correspond a point and a linear space R_k of R_5 and inversely.

The double straight lines of a $(k^2)_4$ of V_∞ envelop a conic; two of those double lines pass through R , hence the image of all double lines through R has 2 points in common with an arbitrary R_4 ; it is a conic k_1^2 . To γ^2 there corresponds a point P and to the pencils touching γ^2 in its points of intersection with rays of the plane pencil round R , there correspond the generatrices of the cone K that has P as vertex and k_1^2 as directrix.

All the quadratic surfaces through A_i relative to which P and one of the straight lines q are harmonically conjugated, form a linear system of ∞^3 individuals, an $(O^2)_3$; this cuts V_∞ in a $(k^2)_3$ to which there corresponds an R_3 in R_5 . Considering the quadratic surfaces through A_i relative to which P and R and P and V_∞ are conjugated, it appears that the R_3 's corresponding to *all* the straight lines q , pass through an R_2 and lie in an R_4 . These R_3 's cut the space R_5 in which K lies, in a plane pencil the rays of which by means of the straight lines q are projectively associated to the generatrices of K . It happens three times that the associated elements coincide, hence there exist three O^2 's through A_i that have a straight line q as chord of contact and the polar plane of P relative to such an O^2 passes through q . To a plane pencil (P, π) there belong therefore three rays of Γ or:

the complex Γ of the axes of rotation of the quadratic surfaces of revolution through 4 given points is of the order 3, the complex cones are of the order three, the complex curves of the class three.

§ 4. Algebraically the order of Γ may be found by determining e.g. the complex cone of an arbitrary point. With a view to this I

take this point as the origin of a rectangular system of coordinates. The equation of an arbitrary quadratic surface of revolution is:

$$f(x, y, z) = x^2 + y^2 + z^2 + a(ax + by + cz)^2 + 2Ax + 2By + 2Cz + D = 0.$$

The axis of revolution is defined by the equations:

$$\frac{\partial f}{\partial x} = \frac{\partial f}{\partial y} = \frac{\partial f}{\partial z}$$

$$a \quad b \quad c$$

or

$$\frac{x + A}{a} = \frac{y + B}{b} = \frac{z + C}{c}$$

and passes through O if

$$\frac{A}{a} = \frac{B}{b} = \frac{C}{c} = \beta.$$

Consequently only the axes of the surfaces

$$x^2 + y^2 + z^2 + a(ax + by + cz)^2 + 2\beta(ax + by + cz) + \gamma = 0$$

pass through O .

We only consider O^2 's through the four given points (x_i, y_i, z_i) , hence:

$$x_i^2 + y_i^2 + z_i^2 + a(ax_i + by_i + cz_i)^2 + 2\beta(ax_i + by_i + cz_i) + \gamma = 0;$$

elimination of a , β and γ gives:

$$\begin{vmatrix} x_i^2 + y_i^2 + z_i^2 & (ax_i + by_i + cz_i)^2 & ax_i + by_i + cz_i & 1 \end{vmatrix} = 0$$

As a, b, c are the direction cosines of an axis through O , they are proportional to the coordinates of an arbitrary point of such a straight line. Consequently the equation of the complex cone of O becomes:

$$\begin{vmatrix} x_i^2 + y_i^2 + z_i^2 & (xx_i + yy_i + zz_i)^2 & xx_i + yy_i + zz_i & 1 \end{vmatrix} = 0.$$

In a similar way an equation may be derived defining the rays of Γ in an arbitrary plane.

§ 5. If the origin of a rectangular system is placed at the centre of the sphere through A_i , the equation of the complex of rays in line coordinates may be written:

$$\begin{vmatrix} 0 & p_4 & p_5 & p_6 & 0 \\ P_1^2 & x_1 & y_1 & z_1 & 1 \\ P_2^2 & x_2 & y_2 & z_2 & 1 \\ P_3^2 & x_3 & y_3 & z_3 & 1 \\ P_4^2 & x_4 & y_4 & z_4 & 1 \end{vmatrix} = 0$$

where $P_i = p_1x_i + p_2y_i + p_3z_i$.

§ 6. All the straight lines through the centre M of the sphere B passing through the points A_i , are rays of Γ . Likewise all the straight lines perpendicular to a side plane of the tetrahedron T that has A_i as angular points; for they are axes of the O^2 consisting of that plane and a parallel plane through the 4th angular point. Further any line perpendicular to 2 subtending sides of T belongs to Γ ; they are the axes of the O^2 consisting of the pair of parallel planes through these 2 sides, hence:

the complex Γ has 8 cardinal points: M , the points D_i at infinity of the normals to the side planes and the points at infinity H_j of the normals to the subtending sides of T .

§ 7. If the points A_i revolve round a straight line l , lying in a perpendicular bisector plane of a side of T , 2 of the points A_i describe the same circle; from this follows that l belongs to Γ , or:

the six perpendicular bisector planes of the sides of T are cardinal planes of Γ .

I shall now show, that all the straight lines of V_∞ are double rays of Γ .

§ 8. The axes corresponding to an arbitrary point P of V_∞ belong to a pencil (O^2); they are the straight lines p' conjugated to the polar line p of P relative to γ^2 . The centres of the individuals of the pencil lie on the polar line p of P relative to γ^2 (they belong to the parabolical cylinder of the pencil) and on a conic passing through P and M and intersecting p . The axes through P form consequently a plane pencil in V_∞ and a pencil the plane of which passes through M , hence:

the complex Γ consists of ∞^3 plane pencils of parallel rays lying in the planes of the sheaf round M .

From this there follows that Γ is invariant for any homothetic transformation relative to M ; the complex cones corresponding to the points of a straight line through M , have accordingly the same curve at infinity.

§ 9. All the straight lines of V_∞ belong to Γ , hence the complex curve of an arbitrary plane π touches the l_∞ of its plane. Besides this straight line one more tangent may be drawn to the complex curve out of each point P of this l_∞ ; namely the line of intersection of π with the plane of the pencil of complex rays through P passing through M . Consequently l_∞ is a bi-tangent of the complex curve of π and also of all the planes in which it lies, or:

V_∞ carries a field of double rays of Γ .

§ 10. *The complex curve of an arbitrary plane π is rational; the l_∞ of its plane is its bi-tangent; single tangents are: the lines of intersection of π with the perpendicular bisector planes of T .*

Through its bi-tangent and the six single tangents the complex curve of an arbitrary plane is defined; other tangents may be constructed with the ruler.

§ 11. If the tetrahedon T is cut by V_∞ , we get the well known configuration of a complete quadrilateral. Polarisation of this figure in the absolute polar field gives a complete quadrangle having D as angular points; the straight lines at infinity of the perpendicular bisector planes are the sides and the points H_j are the diagonal points of this quadrangle.

§ 12. In a plane π through one of the points H_j , hence parallel to a normal to 2 subtending sides of T , the complex rays consist of a plane pencil round H_j and the tangents of a parabola. If π passes at the same time through M , it contains also a plane pencil round M , hence also a third plane pencil; as the l_∞ of π is a double ray of Γ , the centre of this third plane pencil lies also on l_∞ .

In a plane π through 2 of the points H_j there lie plane pencils round both these points, hence also a third plane pencil; to this belong the points of intersection of π with the perpendicular bisector planes through the third of the points H_j , hence:

to Γ there belong three bilinear congruences, which have as directrices the join of 2 of the points H_j and the line through the 3rd of the points H_j and M .

If π passes through 2 points H_j and through M , the complex rays in π form the plane pencils round these three points.

In a plane π through one point H_j and two of the points D_i there lie three plane pencils of complex rays round these points. If π passes also through M it is a cardinal plane.

§ 13. Before investigating the planes through a point D_i I shall first consider the complex cone of a point P of the perpendicular m_i out of M to one of the side planes of T . This complex cone is apparently split up into three plane pencils, lying in the perpendicular bisector planes through m_i ; m_i is a threefold generatrix of the complex cone of each of its points, hence:

the four straight lines m_i are 3 fold rays of Γ .

In a plane π through m_i lies a plane pencil round M and a plane pencil round D_i ; now the l_∞ of π is a double ray and m_i is a

threefold ray of Γ , hence the third plane pencil in π has likewise D_i as vertex; the complex rays in π form accordingly a plane pencil round M and a plane pencil round D_i which is to be counted double.

§ 14. Consider an arbitrary plane π through one of the points D_i ; in this there lies a *plane pencil* of complex rays round D_i , while the rest of the rays envelop a *parabola*. Out of each point P of the l_∞ of π there can be drawn besides l_∞ one more tangent to the parabola; P is the point of contact if this straight line coincides with l_∞ . The plane of the pencil of complex rays through P passes in this case through M and through D_i , hence through m_i , but then P coincides with D_i or:

in a plane through one of the points D_i (\parallel to a straight line m_i) the complex rays consist of a plane pencil round this point and of the tangents of a parabola with axis $\parallel m_i$.

§ 15. In a plane through M there lies a plane pencil of rays round this point and as the l_∞ of this plane p is a double ray of Γ there lie 2 more plane pencils with centres P on p . The points P and the straight lines p are conjugated in a null system [2,1]. By conjugating to each other the points P lying on the same straight line, an involution of pairs [2] arises. This involution is quadratic, for on an arbitrary straight line there lies one pair of conjugated points.

The involution [2] is not a quadratic inversion as the joins of conjugated points do not pass through a fixed point; consequently [2] consists of the pairs of points conjugated to each other relative to the conics of a pencil. This involution has 4 *double points* (the base points of the pencil), in this case the points D_i , and 3 *cardinal points*, the diagonal points of the complete quadrangle of the base points, in our case the points H_i , hence:

the complex Γ consists of pairs of plane pencils of parallel rays lying in planes through M . The vertices of the two plane pencils lying in the same plane, are conjugated points of a quadratic involution in V_∞ .

§ 16. If a straight line p of V_∞ revolves round one of its points O , the points associated to p in the null system [2,1] describe a curve k^3 of the 3rd order; this curve passes through O , through H_j and touches the straight lines OD_i at D_i . The curves k^3 belonging to all the plane pencils of V_∞ , form a net with seven base points, H_j and D_i .

§ 17. In order to get the complex cone of an arbitrary point P , we consider a plane π through MP ; let O be the intersection of MP , p the intersection of π with V_∞ . If P_1 and P_2 correspond to p , PO , PP_1 and PP_2 are the lines of intersection of the complex cone of P with π . If π revolves round PO it appears that:

the complex cone of a point P passes through the straight lines PM and PH_j and touches the planes MPD_i along the lines PD_i .

At the same time it appears again that if P moves along a straight line through M , the curve at infinity of the complex cone of P remains unaltered (cf. § 8).

§ 18. Out of a point O , 4 real tangents OD_i may be drawn to the corresponding curve k^3 , hence the curves k^3 and also the complex cones consist of two parts.

The characteristic of a curve k^3 is defined by the 4 straight lines OD_i . Through D_i there pass 3 conics through the points O of which there pass 4 harmonical rays through D_i , hence:

the locus of the points with harmonical complex cones consists of 3 quadratic cones the vertices of which lie in M and which pass through the straight lines m_i , and also:

the complex cones of the points lying on a quadratic cone through the 4 straight lines m_i , have the same characteristic.

§ 19. The curve of JACOBI of the net of the curves k^3 consists of the six sides of the complete quadrangle of the points D_i . No rational curves k^3 belong to the net, only curves degenerated in a side of the quadrangle and a conic through the 4 points D_i and H_j that do not lie on this side, accordingly:

there are no points with rational complex cones; for any point of a perpendicular bisector plane the complex cone degenerates into a plane pencil and a quadratic cone; for a point V_∞ the complex cone consists of a plane pencil in V_∞ , to be counted double, and a single plane pencil.

§ 20. As each complex curve has a double tangent, we might call those planes where the double tangent is an inflexional tangent, *singular planes*. In this case the two points P corresponding to the straight line p in the null system [2,1], must coincide. This happens only when a plane π passes through one of the points D_i , but then the system of complex rays in π splits up into a plane pencil and the tangents of a parabola; consequently non-degenerate complex curves with an inflexional tangent do not occur.

§ 21. If in π there lies a plane pencil with centre P at finite distance, there are also 2 plane pencils with their centres on the l_∞ of π ; if π does not pass through one of the cardinal points at infinity, the planes of these latter pencils pass through M , hence:
only the planes through the 8 cardinal points contain degenerate complex curves (cf. §§ 12, 13 and 14).

§ 22. As the null system [2,1] and the involution [2] are invariant for central projection, we can *construct the complex cone* of an arbitrary point P in the following way:

We determine the points of intersection D_i of the perpendiculars out of P to the side planes of T with an arbitrary image plane τ and also the intersection O of TM with τ . Then we construct the double points of the quadratic involution in which the conics of the pencil through D_i cut an arbitrary straight line l through O ; we fix this involution by means of the points of intersection of l with 2 degenerate conics of this pencil. The straight lines joining P to the double points in question, are generatrices of the complex cone of P .

§ 23. If the points A_i are coplanar, their plane α cuts an O^2 of the system in consideration along a conic k^2 through A_i or is a part of the O^2 . In the first case the axis of O^2 lies in one of the planes through the axes of symmetry of k^2 perpendicular to α ; in the second case the axis of O^2 is a straight line perpendicular to α . The axes of symmetry of the conics through A_i are tangents to a curve of the 3rd class touching the line l_∞ of α twice; the planes through these axes and $\perp \alpha$ touch a cylinder of the 3rd class with V_∞ as double tangent plane.

The rays of Γ in an arbitrary plane π touch also in this case at a curve of the 3rd class that has the l_∞ of its plane as a bitangent. The complex cone of an arbitrary point P , however, splits up into 3 plane pencils the planes of which touch at the cylinder in question; a perpendicular to α is a triple generatrix of the complex cone of each of its points, hence:

if the 4 points A_i are coplanar, Γ consists of the tangents to a cylinder of the 3rd class; V_∞ is the bearer of a field of double rays; the vertex of the cylinder at infinity is the bearer of a sheaf of triple rays.

§ 24. Now consider the case that 3 of the points A_i lie on a straight line a ; then the O^2 's must pass through a fixed point A

and a fixed straight line a . If A is to lie on the quadratic surface which a describes when it revolves round a straight line l , the circle which A describes when it revolves round l , must cut the straight line a ; accordingly l must lie in the plane which bisects perpendicularly the straight line joining A to a point of a . These planes touch a parabolical cylinder that has for directrix the parabola of which A is the focus and a the director line and the generatrices of which are perpendicular to the plane (A, a) .

If a revolves round a straight line crossing it at right angles, a plane is produced which, completed by the plane through A parallel to it, gives another O^2 that satisfies the conditions mentioned, hence:

if three of the four points A_i are collinear, Γ splits up into a pencil of rays with the axis at infinity, and the tangents to a parabolical cylinder.

Mathematics. — “*Axes of Rotation and Planes of Symmetry of Quadratic Surfaces of Revolution through 5, 6 and 7 Given Points.*” By H. J. VAN VEEN. (Communicated by Prof. JAN DE VRIES).

(Communicated at the meeting of April 29, 1922).

§ 1. Let there be given five points A_1, A_2, B_j ($j = 1, 2, 3$). I consider the complexes Γ_1 and Γ_2 belonging to the points A_1, B_j and A_2, B_j ¹⁾. Generally a common ray l of Γ_1 and Γ_2 is the axis of an O^2 through the 5 points; for l is the axis of an O^2 through A_1, B_j and of an O^2 through A_2, B_j ; these two O^2 's have in common the 3 parallel circles on which the B_j lie; hence they coincide. An exception exists for the straight lines in the perpendicular bisector plane of the join of 2 of the points B_j , and also for the straight lines of V_∞ . The field degree of the congruence of axes is therefore

$$3 \cdot 3 - 3 - 2 \cdot 2 = 2.$$

At the same time there must be split off: the sheaf of the rays which are perpendicular to the plane through the points B_j . Let D be the centre at infinity of this sheaf; both the complex cones of a point P touch the plane through P, M_1, M_2 and D along P, D , hence:

the axes of the O^2 's through 5 given points form a congruence of the sheaf degree 7 and the field degree 2, $C^{7,2}$.

§ 2. To $C^{7,2}$ belong the complex rays of Γ_2 lying in the perpendicular bisector plane of a straight line A_1, B_j , hence:

the 10 perpendicular bisector planes of the joins of the 5 given points are singular planes of the order 3.

§ 3. In the two null systems belonging to Γ_1 and Γ_2 the curves k_1^3 and k_2^3 (O^2 's through 4 points § 16) are associated to a plane pencil round a point O of V_∞ ; these curves pass through O , touch OD at D and have accordingly six more points in common. Consequently through O there pass six straight lines on which the two pairs of points which through the two null systems are associated to them, have one point in common.

¹⁾ Cf. my paper “*Axes of Rotation of Quadratic Surfaces through 4 Given Points.*”

The complex curves in an arbitrary plane through such a straight line touch each other at the point in question, so that the two complex curves have 5 coinciding tangents in common in the l_∞ of their plane. Now we have split off the straight lines of V_∞ as 4-fold rays of the congruence of the intersection of the two complexes, hence:

V_∞ is a singular plane of the order 6.

§ 4. We can also arrive at this last result in the following way. The quadratic surfaces through 5 points form a linear system of ∞^1 individuals; these cut V_∞ in a $(k^2)_4$; the conic of the double straight lines of this $(k^2)_4$ belongs to the parabolical cylinders of $(O^2)_4$. Let C be such a cylinder, T its vertex, c the line along which C touches V_∞ .

The polar plane of T relative to C is indefinite, hence T has a fixed polar plane relative to all O^2 's of the pencil through $A_1 B_j$, which touch γ^2 in its points of intersection with c . This fixed polar plane is at the same time the plane of the centres of the individuals of the pencil; it passes through the polar line p of T relative to γ^2 . In the null system [2,1] belonging to Γ_1 the pole P of c relative to γ^2 is associated to p .

As the fixed polar plane of T relative to the O^2 's through $A_2 B_j$ that touch γ^2 at its points of intersection with c , pass likewise through p , in the two null systems corresponding to Γ_1 and Γ_2 the point P is associated to p .

P was the pole of c relative to γ^2 , hence the locus of P is a conic. The order of the null systems is three; accordingly the locus of the straight line p is a curve of the sixth class.

We remark also that to each parabolical cylinder one axis in V_∞ remains associated (O^2 's through 4 points, § 2), namely the polar line of its vertex relative to γ^2 .

§ 5. If six points are given I consider a group of 4 and a group of 5 of these points which have 3 points in common. To the group of 4 points there belongs a complex I^3 , to that of 5 points a congruence $C^{7,2}$. The axes in question are part of the common rays of complex and congruence; however, we must split off: the tangents of three curves of the 3rd class and twice the tangents of a curve of the sixth class, so that we arrive at a ruled surface of the order $3(7 + 2) - 3 \cdot 3 - 2 \cdot 6 = 6$, hence:

the axes of the O^2 's through six points form a ruled surface of the sixth order, ϱ^6 .

§ 6. Through consideration of the perpendicular bisector plane of the straight line through the 2 points that belong to the group of 5 and not to the group of 4 points, we find that in this plane and accordingly in each of the 15 perpendicular bisector planes, there lie 2 generatrices of ϱ^6 .

The quadratic surfaces through six points cut V_∞ in a linear system of ∞^3 conics $(k^3)_3$. These define together with γ^2 a linear system $(k^2)_4$; the tangents of the conic of the double lines of $(k^2)_4$ are the chords of contact of the O^2 's through the six points; polarisation of these straight lines relative to γ^2 gives a conic k^2 ; to $(k^2)_3$ there belong four double lines, originating from parabolical cylinders (cf. § 4), so that the locus of the axes has a conic k^2 and 4 straight lines in common with V_∞ , hence:

ϱ^6 is rational; it has a double curve of the order 10; the 15 perpendicular bisector planes of the joins of the six points are bi-tangent planes; V_∞ is a 4-fold tangent plane.

§ 7. In order to investigate the axes of the O^2 's through seven points, we consider a group of 4 and a group of 6 of these points that have 3 points in common. We get in this way a complex F_3 and a ruled surface ϱ^6 that have 18 straight lines in common. If we subtract from them three times two straight lines lying in the perpendicular bisector planes of the joins of the 3 common points, and twice 4 straight lines in V_∞ , we have 4 straight lines left, hence:

through 7 points there pass 4 O^2 's.

§ 8. We can also arrive at this result in the following way. All quadratic surfaces through 7 points cut V_∞ in a $(k^2)_2$; in connection with γ^2 this gives a $(k^2)_3$ with 4 double straight lines, consequently in $(k^2)_3$ there are four individuals touching γ^2 twice. These belong to the surfaces of rotation through the 7 points.

§ 9. A quadratic surface of revolution O^2 has a pencil of planes of symmetry passing through the axis of rotation and therefore defined together with this axis, and further generally one more plane of symmetry perpendicular to the axis. I shall investigate these latter planes for O^2 's through given points and I define as a *plane of symmetry* of an O^2 the polar plane of the point P at infinity of the axis of rotation; if this polar plane is indefinite the planes through the chord of contact p of the O^2 are considered as planes of symmetry.

§ 10. An arbitrary plane π is a plane of symmetry of one O^2 through *four* given points A_i ; for through A_i there passes a pencil of O^2 's touching γ^2 at its points of intersection with π ; generally one of these O^2 's passes through the mirror image of one of the points A_i relative to π and this surface satisfies the conditions.

It may happen that the mirror image in question lies on the base curve of the pencil; then π is a plane of symmetry of all individuals of the pencil. As the sphere B through A_i belongs to the pencil, π must pass in this case through the centre M of this sphere.

§ 11. The ∞^2 planes of symmetry of the O^2 's through *five* points envelop a surface of which I shall determine the class. The O^2 's the planes of symmetry of which pass through a point P of V_∞ , cut V_∞ along conics that touch γ^2 at its points of intersection with a ray of the plane pencil round P . The image of all such conics in R_4 is a quadratic cone K (O^2 's through 4 points § 3).

The quadratic surfaces through the 5 given points cut into V_∞ a $(k^2)_4$ that has an R_4 as image in R_5 ; this R_4 cuts K along a conic k^2_{II} .

To the degenerate conics of V_∞ there corresponds in R_5 a *cubic hypersurface*, V^3_4 , that has a *double surface* O^4_2 of the 4th order (a surface of *Veronese*). Besides its two points of intersection with k^2_I (O^2 's through 4 points, § 3) that lie on O^4_2 , k^2_{II} has 2 more points in common with V^3_4 , hence to the O^2 's through the 5 given points the planes of symmetry of which pass through P , there belong *two paraboloids of revolution*; these have V_∞ as a plane of symmetry. Through a ray ρ of the plane pencil round P there passes one more plane of symmetry that does not coincide with V_∞ , consequently the planes of symmetry through P envelop a cone that has P for vertex and that touches V_∞ twice. An arbitrary straight line l through P bears therefore 3 planes of symmetry; through a line of V_∞ there passes besides V_∞ only one more plane of symmetry, hence:

the planes of symmetry of the O^2 's through 5 given points envelop a surface of the 3rd class of which V_∞ is a double-tangent plane.

§ 12. The conic along which this surface touches V_∞ , has six tangents that are the bearers of pencils of tangent planes; these cannot belong to different O^2 's for in that case through the 5 given points there would pass a pencil of O^2 's touching γ^2 at its points of intersection with a straight line ρ and from this would follow that the 5 given points must lie on a sphere.

To each of the six straight lines p belongs therefore one O^2 that has a pencil of parallel planes of symmetry, or:

through 5 given points there pass six cylinders of revolution; their generatrices are parallel to 6 sides of a quadratic cone.

§ 13. The planes of symmetry through an arbitrary point touch a cone of the 3rd class; let π be such a plane through the centre M of the sphere B through 4 of the 5 given points; π is then a plane of symmetry of an O^2 through the 5 points and also of the sphere B , hence of a pencil of O^2 's through those 4 points, or:

through the centre of the sphere through 4 given points there pass ∞^1 planes each of which is a plane of symmetry of a pencil of O^2 's through those 4 points; these planes envelop a cone of the 3rd class.

Such a plane π is also a plane of symmetry of the base curve of the corresponding pencil, consequently to this pencil there belongs a cylinder of revolution of which the generatrices are perpendicular to π , hence:

through 4 points there pass ∞^1 cylinders of revolution of which the generatrices are parallel to the generatrices of a cone of the 3rd order.

§ 14. If six points are given, we consider two groups of five points; these have 4 points in common. The surfaces of the 3rd class corresponding to these two groups, have in common the tangent planes of a developable surface of the 9th class that has V_∞ as a 4-fold tangent plane. However, we must subtract from this the tangent planes through the centre of the sphere through the 4 common points, hence:

the planes of symmetry of the O^2 's through six given points envelop a developable surface of the 6th class that has V_∞ as a 4-fold tangent plane.

§ 15. The quadratic surfaces through six points cut V_∞ in a $(k^2)_3$; to this there belong 4 double straight lines; how many degenerate curves touching γ^2 twice, belong to $(k^2)_3$?

In order to determine this number we remark that the cone in R_4 formed by the straight lines joining the image of γ^2 to O^4 , (§ 11), cuts the image R_3 of $(k^2)_3$ along a curve k^4 of the 4th order; this curve has besides the 4 points that are the images of the double lines of $(k^2)_3$ and that are to be counted twice, 4 more points in common with V_∞ , hence:

through six points there pass 4 parabolical cylinders and 4 paraboloids of revolution.

As through an arbitrary point P of V_∞ there pass 2 more planes of symmetry, (for the conic of the double lines of $(k^2)_4$ defined by γ^2 and $(k^2)_3$ sends two of them through P), we find also in this way, that the planes of symmetry in consideration envelop a developable surface of the sixth class with V_∞ as a 4-fold tangent plane.

§ 16. In order to find the planes of symmetry through *seven* given points, we consider a group of six and a group of five of these points that have 4 points in common. The corresponding surfaces have $3 \cdot 6 = 18$ tangent planes in common. If we subtract from them $2 \cdot 4 = 8$ times V_∞ and further 6 planes through the centre of the sphere through the 4 common points, it appears again that:

through seven given points there pass 4 quadratic surfaces of revolution.

(Cf. §§ 7 and 8).

Physics — “*A Connection between the Spectra of Ionized Potassium and Argon.*” (First Communication.) By Prof. P. ZEEMAN and H. W. J. DIK.

(Communicated at the meeting of April 29, 1922).

According to the conception of RUTHERFORD-BOHR an atom consists of a very small positively charged nucleus, which contains almost the whole mass of the atom, and of a number of electrons revolving round the nucleus. The number of electrons moving round the nucleus, is equal to the atomic number of the element; hence this also indicates the number of units of charge which an atom that is neutral taken as a whole, possesses in the nucleus.

It has been made plausible that the electrons are arranged in shells or sheaths with the nucleus as centre. In particular the regular changes which the chemical properties undergo with the increase of the atomic number, make this probable. Regularly elements occur in the periodic system which easily cede one electron (the alkalis), regular is also the succession of the inert gases. This becomes comprehensible when it is assumed that a shell can become full, and that then the configuration will be very stable: helium, neon, argon etc. The atoms of lithium, sodium, potassium etc. have only one electron in the outer shell. On this similarity in structure rests also the resemblance which has been observed at an early date in the arc-spectra of the alkalis. The one outer electron can be removed by the electric forces which are active in a spark. Then the atom is ionized, and the electron combination which has remained, can emit the spark spectrum.

On these general features of the atomic model, in particular on the number of outer electrons which increases at every step in the periodic system, rests a displacement law enunciated by KOSSEL and SOMMERFELD¹⁾, which establishes a connection between the spark spectrum of an element and the arc-spectrum of another element which precedes it in the periodic system. If e.g. an electron of the potassium-atom has been driven out, the remaining electron system must present the greatest resemblance with that of argon, and only

¹⁾ KOSSEL u. SOMMERFELD, Auswahlprincip und Verschiebungssatz bei Serienspektren. Verh deutsch. physik. Gesellsch. 21. Jahrgang 240, 1919.

differ from it in that the positive nucleus of potassium possesses one unit of charge more. Like the arc-spectrum of argon, the spark-spectrum of potassium must be composed of a great number of lines, and not show series. As yet the relation which the displacement law renders probable, is only qualitatively known.

For some time some researches have been in progress in the Amsterdam laboratory to determine the relation quantitatively.

We will here communicate some results to which the investigation of *potassium* has led. These facts retain their value whatever interpretation may have to be given to them.

Besides the arc-spectrum of potassium with the so well-known spectrum series which according to SOMMERFELD's opinion originates from the neutral atom, EDER and VALENTA¹⁾ observed in 1894 a spectrum, emitted by ionized potassium, which was very rich in lines. EDER and VALENTA observed simultaneously arc- and spark lines; in 1907 GOLDSTEIN²⁾ however, succeeded in observing in the intensely luminous line of discharge occurring in the passage of vigorous electric discharges through powdered salts, a spectrum in which only lines are seen which have not been ranged into series, and in which even the distinct arc-lines did not appear. GOLDSTEIN points out that these lines owe their origin to circumstances which differ essentially from those which give rise to the arc-lines, and he introduces the name of "ground" spectrum. We are undoubtedly justified in attributing the ground spectra to the emission of the once ionized atom.

In the subjoined Table I a * denotes the strongest lines, those published by GOLDSTEIN.

With better appliances EDER's pupil SCHILLINGER³⁾ could supplement GOLDSTEIN's observations by investigating also the ultra-violet. He worked with vigorous discharges between potassium electrodes in a bulb with hydrogen. His observations are given under S in Table I.

In 1915 some observations of NELTHORPE⁴⁾ were published for potassium lying between 6307 Å and 3898 Å. He employed another type of tube than GOLDSTEIN, and recorded by means of a spectrograph. On his plates the arc-lines are absent, the ground-spectrum of GOLDSTEIN coinciding with his strongest lines. The doubt expressed by KAYSER whether GOLDSTEIN's failure to see the

1) EDER u. VALENTA, Denkschriften Wien. Akad. **61**. 347, 1894.

2) GOLDSTEIN, Verh. deutsch. physik. Ges. 321. 1907; 426, 1910.

3) SCHILLINGER, Wiener Sitz. Ber. **118** [2a] 605. 1909.

4) NELTHORPE. Astroph. Journ. **41**. 16. 1909.

TABLE I. Potassium lines with electrode less discharge.

| EV | Intensity. | | | | λ | ν | Remarks |
|----|------------|---|-----|----|------------|-------------|----------------|
| | S | N | McL | D | | | |
| 8 | 5 | | | | 7699.4 | | Arc-line |
| 8 | 5 | | | | 7665.6 | | • |
| 8 | 6 | | | | 6938.9 | | • |
| 7 | 4 | | | — | 6911.3 | | • |
| — | — | | — | 1 | \pm 6594 | \pm 15165 | P ₁ |
| — | — | | — | 2 | \pm 6562 | | H 6563? |
| — | 1 | — | | 1 | 6427.9 | 15557 | |
| — | 2 | 3 | | 8 | 6307.2 * | 15855 | |
| — | 1 | 1 | | 5 | 6246.5 * | 16009 | Q ₁ |
| — | 2 | 8 | | 15 | 6120.2 * | 16340 | P ₂ |
| — | — | — | 3 | — | 6050 | | |
| 3 | 4 | — | | — | 5832.2 | | Arc-line |
| 3 | 2 | — | | — | 5812.5 | | • |
| 4 | 5 | — | | — | 5802.0 | | • |
| 3 | 3 | — | | — | 5782.6 | | • |
| — | — | — | — | 1 | \pm 5772 | 17324 | |
| — | — | — | 2 | — | 5730 | | |
| — | — | — | | 3 | \pm 5645 | 17715 | S ₁ |
| — | — | — | — | 1 | \pm 5536 | 18064 | R ₂ |
| — | — | — | — | 4 | 5469 | 18286 | P ₃ |
| 8 | 2 | — | | — | 5359.9 | | Arc-line |
| 1 | 1 | — | | — | 5343.3 | | • |
| 8 | 2 | — | | — | 5340.0 | | • |
| 2 | 1 | — | | — | 5323.6 | | • |
| — | — | — | — | 3 | 5314 | 18817 | |
| 2 | 1 | — | | — | 5112.7 | | Arc-line |
| 2 | 1 | — | | — | 5099.6 | | • |
| 1 | 1 | — | | — | 5085.1 | | • |
| 1 | 1 | — | | 8 | 5056.0 | 19778 | P ₄ |

TABLE I (Continued).

| EV | Intensity. | | | | λ | ν | Remarks. |
|----|------------|----|-----|----|------------|-------|-----------------|
| | S | N | McL | D | | | |
| 2 | 2 | 5 | | 15 | 5005.5 * | 19978 | R ₃ |
| 1 | — | — | — | | 4965.5 | | Arc-line |
| — | — | — | — | | 4958 | | • |
| 1 | 1 | — | | 5 | 4943.2 | 20230 | P ₅ |
| — | — | — | 3 | — | 4863 | | Arc-line |
| 3 | 2 | 12 | | 30 | 4829.2 * | 20707 | |
| — | — | — | 1 | — | 4805 | | Arc-line |
| — | — | — | 1 | — | 4790 | | • |
| — | — | — | 1 | — | 4769 | | |
| — | — | — | 1 | — | 4760 | | • |
| — | — | — | 1 | 3 | 4744 | 21079 | Q ₅ |
| — | — | — | 1 | — | 4720 | | |
| — | — | — | 1 | — | 4688 | | |
| 3 | 1 | — | | 15 | 4659.8 | 21460 | R ₄ |
| 2 | — | — | — | — | 4650.7 | | |
| — | — | — | 1 | — | 4643 | | Arc-line |
| 6 | 4 | 15 | | 30 | 4608.5 * | 21699 | |
| — | — | — | — | 10 | 4596.0 | 21758 | P ₆ |
| 5 | 4 | 8 | | 30 | 4505.6 * | 22195 | P ₇ |
| 5 | 2 | 5 | | 20 | 4467.5 * | 22384 | P ₈ |
| 1 | — | — | 2 | 9 | 4455.5 | 22444 | P ₉ |
| 1 | 1 | 1 | | 10 | 4423.6 | 22606 | Q ₆ |
| 3 | 3 | 10 | | 30 | 4388.3 * | 22788 | |
| — | — | — | 2 | 10 | 4365.1 | 22909 | P ₁₂ |
| — | 1 | 5 | | 30 | 4339.9 | 23042 | Q ₇ |
| 1 | 5 | ? | | 30 | 4309.5 } • | 23204 | P ₁₃ |
| 2 | 3 | 4 | | 30 | 4305.0 } | 23229 | Q ₈ |
| — | 1 | — | | 9 | 4288.6 | 23317 | |
| — | — | — | — | 8 | 4285.1 | 23337 | Q ₁₀ |

TABLE I (Continued).

| Intensity. | | | | | λ | ν | Remarks. |
|------------|----|----|-----|----|------------|-------|--------------------------------|
| EV | S | N | McL | D | | | |
| 6 | 8 | 10 | | 30 | 4263.5 * | 23455 | R ₆ |
| 6 | 4 | 6 | | 30 | 4225.7 } * | 23665 | Q ₁₁ |
| 6 | 5 | 8 | | 30 | 4223.2 | 23679 | |
| 1 | 1 | — | | 9 | 4208.9 | 23759 | Q ₁₂ |
| 8 | 10 | 20 | | 30 | 4186.2 * | 23888 | R ₇ |
| 6 | 5 | 10 | | 30 | 4149.1 * | 24102 | P ₁₄ |
| 6 | 5 | 10 | | 30 | 4134.7 * | 24185 | R ₁₀ |
| 4 | 3 | 10 | | 30 | 4115.1 * | 24301 | S ₆ |
| — | — | 5 | — | — | 4106.8 | | |
| — | — | 7 | 1 | — | 4104.2 | | |
| — | — | 3 | — | — | 4098.6 | | |
| — | 1 | 2 | | 15 | 4093.5 | 24429 | P ₁₅ |
| — | — | 2 | — | — | 4086.8 | | |
| — | — | 3 | — | — | 4075.6 | | |
| — | — | 2 | — | — | 4072.3 | | |
| — | 1 | 1 | | 10 | 4065.2 | 24599 | R ₁₂ |
| — | 2 | 7 | | — | 4058.1 | | |
| 10 | 10 | — | | — | 4047.4 | | Arc-line |
| 10 | 20 | — | | — | 4044.3 | | Arc-line |
| — | 2 | 5 | | 15 | 4042.5 | 24737 | P ₁₇ S ₇ |
| 1 | 1 | — | | 10 | 4039.9 | 24753 | |
| 1 | 1 | — | | 10 | 4024.9 | 24845 | P ₁₈ |
| 1 | 1 | 4 | | 9 | 4018.9 | 24882 | P ₁₉ |
| 2 | 1 | 1 | | 10 | 4012.2 | 24924 | S ₈ |
| 6 | 5 | 8 | | 15 | 4001.1 | 24993 | P ₂₀ S ₉ |
| 1 | 4 | 3 | | 10 | 3995.0 | 25031 | S ₁₀ |
| — | — | — | | 8 | 3992.0 | 25050 | P ₂₁ |
| 3 | 3 | 4 | | 15 | 3972.8 | 25171 | P ₂₂ |
| | 3 | 3 | | 15 | 3966.7 | 25210 | P ₂₃ |

TABLE I (Continued).

| Intensity. | | | | | λ | ν | Remarks. |
|------------|---|----|-----|----|-----------|-------|---------------------------------|
| EV | S | N | McL | D | | | |
| 4 | 4 | 8 | | 15 | 3955.5 | 25281 | Q ₁₅ |
| 2 | 1 | 4 | | 10 | 3943.3 | 25359 | S ₁₁ |
| 1 | 1 | 1 | | 9 | 3934.6 | 25416 | |
| 1 | 1 | 2 | | 9 | 3927.3 | 25463 | S ₁₂ |
| 1 | 1 | — | | 9 | 3923.8 | 25485 | P ₂₄ |
| 8 | 8 | 10 | | 15 | 3898.0 | 25654 | |
| — | — | | | 3 | 3887.2 | 25726 | Q ₁₉ |
| 1 | — | | | 5 | 3884.5 | 25743 | S ₁₃ |
| 1 | 1 | | | 8 | 3879.2 | 25779 | P ₂₅ |
| 2 | 1 | | | 10 | 3874.5 | 25810 | R ₁₄ |
| 1 | 1 | | | 10 | 3861.9 | 25894 | Q ₂₁ |
| — | — | | | 3 | 3844.8 | 26009 | P ₂₆ |
| 1 | 2 | | | 15 | 3818.6 | 26187 | P ₂₇ |
| | 1 | | | — | 3816.9 | | |
| 1 | 2 | | | 15 | 3800.8 | 26310 | R ₁₆ |
| 3 | 3 | | | 15 | 3783.2 | 26433 | R ₁₇ |
| 1 | 3 | | | 15 | 3767.1 | 26546 | R ₁₈ |
| 1 | 1 | | | 6 | 3756.0 | 26624 | Q ₂₅ |
| 1 | — | | | — | 3749.1 | | |
| 1 | 1 | | | 9 | 3745.2 | 26701 | R ₂₀ |
| 1 | 1 | | | 9 | 3739.2 | 26744 | R ₂₁ |
| 1 | — | | | — | 3727.5 | | |
| — | 1 | | | 9 | 3722.1 | 26866 | R ₂₂ |
| 1 | 1 | | | 9 | 3716.9 | 26904 | R ₂₃ |
| 1 | — | | | — | 3713.2 | | |
| — | 1 | | | — | 3683.7 | | |
| 4 | 4 | | | 15 | 3682.3 | 27157 | S ₁₆ |
| — | 1 | | | 8 | 3677.6 | 27192 | P ₂₉ R ₂₄ |
| 1 | 1 | | | 10 | 3670.2 | 27246 | P ₃₀ |

TABLE I (Continued).

| Intensity. | | | | | λ | ν | Remarks. |
|------------|---|---|------|----|-----------|-------|---------------------------------|
| EV | S | N | McL | D | | | |
| — | — | | 4 d. | — | 3660 | | |
| — | — | | — | 1 | 3650.6 | 27393 | S ₁₈ |
| — | 1 | | | 4 | 3639.8 | 27474 | R ₂₅ |
| — | 1 | | | 9 | 3627.1 | 27570 | Q ₂₈ |
| 3 | 2 | | | 15 | 3618.4 | 27636 | P ₃₁ |
| 2 | 3 | | | 12 | 3609.4 | 27705 | R ₂₆ |
| — | — | | 1 | 2 | 3593.8 | 27826 | |
| — | — | | 1 | 2 | 3587.1 | 27878 | R ₂₇ |
| — | — | | 1 | — | 3572 | | |
| — | 1 | | | 8 | 3562.5 | 28070 | P ₃₂ |
| 2 | 3 | | | 20 | 3530.9 | 28321 | S ₂₅ |
| — | 1 | | | 7 | 3518.8 | 28419 | R ₂₈ |
| — | 1 | | | 7 | 3514.0 | 28458 | P ₃₃ |
| — | — | | 1 | — | 3489 | | |
| 1 | 1 | | | 8 | 3481.3 | 28725 | P ₃₅ S ₂₇ |
| 1 | 1 | | | 8 | 3476.9 | 28761 | |
| — | 1 | | | 7 | 3468.7 | 28830 | P ₃₆ |
| — | — | | — | 2 | 3457.8 | 28920 | Q ₃₂ |
| 10 | 2 | | | 1 | 3447.5 | 29006 | Arc-line |
| | 3 | | | — | 3446.5 | | » |
| 6 | 3 | | | 12 | 3440.5 | 29065 | |
| 1 | 2 | | | 10 | 3433.7 | 29123 | P ₃₇ |
| — | 1 | | | 8 | 3422.4 | 29219 | |
| 1 | — | | — | 4 | 3421.5 | 29227 | |
| 2 | 2 | | | 10 | 3404.7 | 29371 | P ₃₈ |
| — | 1 | | | 7 | 3393.2 | 29471 | P ₃₉ |
| 6 | 4 | | | 10 | 3385.3 | 29539 | Q ₃₄ |
| 6 | 4 | | | 10 | 3381.4 | 29573 | Q ₃₅ |
| 1 | 3 | | | 10 | 3374.0 | 29638 | P ₄₀ |

TABLE I (Continued).

| Intensity. | | | | | λ | ν | Remarks. |
|------------|---|---|-----|----|-----------|-------|-----------------|
| EV | S | N | McL | D | | | |
| — | 6 | | | 15 | 3364.7 | 29720 | |
| 1 | 8 | | | | 3363.4 | 29732 | S ₂₉ |
| — | 2 | | | 7 | 3359.1 | 29770 | R ₃₂ |
| | 2 | | | 7 | 3357.2 | 29787 | S ₃₀ |
| 8 | 5 | | 6 | 12 | 3345.8 | 29888 | P ₄₁ |
| — | — | | 3 | 1 | 3337.7 | 29961 | |
| 1 | — | | — | — | 3326.4 | | |
| 1 | 4 | | 3 | 9 | 3322.1 | 30101 | P ₄₂ |
| 3 | 4 | | 5 | 9 | 3312.8 | 30186 | S ₃₁ |
| — | — | | 3 | 7 | 3302.0 | 30284 | |
| 3 | 3 | | 5 | 9 | 3291.1 | 30385 | R ₃₄ |
| — | 4 | | — | 9 | 3289.1 | 30404 | |
| — | 3 | | 3 | 7 | 3278.8 | 30499 | P ₄₃ |
| | 2 | | 3 | 6 | 3262.0 | 30656 | |
| — | — | | 3 | 1 | 3258.8 | 30686 | |
| — | — | | — | 2 | 3253.9 | 30732 | Q ₄₁ |
| — | 2 | | 3 | 6 | 3241.1 | 30854 | |
| 1 | 1 | | 1 | 5 | 3224.8 | 31010 | S ₃₃ |
| 2 | 2 | | — | 8 | 3220.9 | 31047 | |
| | 1 | | — | 1 | 3219.1 | 31064 | R ₃₈ |
| 2 | 1 | | — | — | 3217.5 | | Arc-line |
| 1 | 4 | | — | 5 | 3209.1 | 31161 | R ₃₉ |
| — | — | | 4 | — | 3205.6 | | |
| 1 | 3 | | — | 6 | 3202.1 | 31230 | S ₃₄ |
| 2 | 2 | | — | 6 | 3190.6 | 31342 | R ₄₀ |
| — | 2 | | 5 | 6 | 3188.3 | 31365 | S ₃₆ |
| — | — | | 2 | — | 3174.0 | | |
| 1 | 1 | | 4 | 3 | 3170.0 | 31546 | |
| 1 | 1 | | 3 | 1 | 3157.6 | 31670 | S ₃₇ |

TABLE I (Continued)

| Intensity. | | | | | λ | ν | Remarks. |
|------------|---|---|-----|---|-----------|-------|-----------------|
| EV | S | N | McL | D | | | |
| — | — | | 2 | — | 3148.6 | | |
| 3 | — | | — | — | 3143.7 | | |
| 4 | 2 | | 4 | 5 | 3129.5 | 31954 | |
| 5 | 4 | | 6 | 6 | 3105.4 | 32202 | R ₁₃ |
| 1 | 1 | | — | — | 3103.1 | | |
| 1 | 1 | | 2 | — | 3074.6 | | |
| 1 | — | | — | — | 3067.3 | | |
| 6 | 5 | | 5 | 5 | 3062.6 | 32652 | S ₄₂ |

said arc-lines might possibly have to be attributed to a less good observational power in the extreme red and violet, appears therefore unfounded.

The importance of the ground spectra made it desirable to perform new measurements. The best method to obtain the first spark spectrum of potassium in great purity and completeness we found to be exciting the luminosity of very diluted incandescent potassium vapour under the influence of very rapidly varying electrical forces.

When our investigation was in progress, there appeared a publication by Mc LENNAN¹⁾ on the spectrum of ionized potassium. His tables present a close resemblance to ours, but in his Table I Mc LENNAN gives the lines which he has observed besides those of SCHILLINGER. Hence he also finds the arc-lines, which we succeeded in eliminating.

Besides both in his and in SCHILLINGER's observations a few important lines are wanting. Important because they have been serviceable in the search for the regularities to be mentioned presently. By the aid of Table I it is possible to compare the measurements of our second (D) with those of the other observers, besides the data in the column "remarks" show which *P, Q*, etc. could only be determined by the new lines. At the same time it is at once clear which of the lines are arc-lines. We estimate the accuracy of the measurements

¹⁾ Mc LENNAN, Proc. R. S. Vol. 100. 182. 1921.

from 4700 Å at 0,2 Å. To some lines a \pm is added to show that they are not sufficiently accurate. (Cf. Table I).

Argon can emit two types of spectra. One is the so-called red spectrum, which is formed under the influence of weak electric forces, and must, therefore, be called the arc-spectrum of argon. The other is formed by strong electric discharges, and is called the blue spectrum because of its colour; it is the spark spectrum of argon. No spectrum series are known in the red spectrum, but it exhibits the regularity found by RYDBERG¹⁾ that for $\lambda < 4704$ Å the frequencies of almost all the lines may be arranged in a Table the four columns of which present a constant difference. PAULSON²⁾ extended these results to the less refrangible part of the spectrum. RYDBERG's and PAULSON's tables are reproduced here in Table II, somewhat abbreviated, but with continuous notation. It gives the constant differences for the wave-lengths of λ 9233—3319 Å. (Cf. Table II). The relations are:

$$B = A + 846,1$$

$$C = A + 1649,3$$

$$D = A + 2256,1$$

The frequencies in Table II followed by an M have been taken from MEGGERS³⁾. They are more accurate than the frequencies in the original tables of RYDBERG and PAULSON. For this reason the mean value of MEGGERS has been put at the head of the Δr -column and not the mean value of all Δr 's.

The spark spectrum of potassium possesses the same property RYDBERG found in argon, for the examined region between 6594—3063 Å. This appears from Table III, which has been obtained by the aid of the data in Table I. Under the heading "Remarks" in Table I the lines inserted and arranged in Table III are indicated by symbols (See Table III).

The relations for the lines of ionized potassium are:

$$Q = P + 847$$

$$R = P + 1695$$

$$S = P + 2542$$

The first spark spectrum of potassium is, therefore, still somewhat simpler than the red spectrum of argon, the differences being:

¹⁾ RYDBERG. On the constitution of the red spectrum of argon. *Astroph. Journ.* Vol. 6. 338. 1897.

²⁾ PAULSON, *Physik. Z. S.* 15. 831. 1914.

³⁾ MEGGERS, *Scientific Papers, Bureau of Standards N^o. 414, 1918*

TABLE II. Arc-Spectrum of Argon. (RYDBERG and PAULSON).

| No. | A | $\Delta\lambda$ 846.2 | B A + 846.2 | $\Delta\lambda$ 803.1 | C A + 1649.3 | $\Delta\lambda$ 606.8 | D A + 2256.1 |
|-----|-----------|--------------------------|----------------|--------------------------|-----------------|--------------------------|-----------------|
| 1 | | | | | 10353.2 | 607.3 | 10960.5 |
| 2 | | | 11533.6 M | 803.1 | 12336.7 M | 606.8 | 12943.5 M |
| 3 | 10837.7 M | | | (1649.3) | 12487.0 M | 606.8 | 13093.8 M |
| 4 | | | 11896.7 | | | (1410.4) | 13307.1 |
| 5 | 11731.9 M | 846.2 | 12578.1 M | | | (1409.9) | 13988.0 M |
| 6 | 11889.9 M | | | (1649.2) | 13539.1 M | 606.8 | 14145.9 M |
| 7 | 12096.6 M | 846.2 | 12942.8 M | 803.0 | 13745.8 M | 606.9 | 14352.7 M |
| 8 | 12477.0 | | | | | (2258.1) | 14735.1 |
| 9 | 13326.2 | | | | | (2258.5) | 15584.7 |
| 10 | | | | | 15012.9 | 606.7 | 15619.6 |
| 11 | 13668.4 | 847.9 | 14516.3 | | | (1410.3) | 15926.6 |
| 12 | | | | | 15429.3 | 606.7 | 16036.0 |
| 13 | 14223.7 | | | (1651.8) | 15875.5 | | |
| 14 | | | 15078.3 | | | (1409.9) | 16488.2 |
| 15 | 14413.4 | | | (1651.2) | 16064.6 | | |
| 16 | | | 15398.6 | | | (1409.6) | 16808.2 |
| 17 | | | | | 16219.8 | 606.9 | 16826.7 |
| 18 | | | | | 16340.6 | 606.5 | 16947.1 |
| 19 | | | 15699.2 | 803.5 | 16502.7 | | |
| 20 | 14972.3 | | | (1651.7) | 16624.0 | | |
| 21 | | | | | 16716.2 | 607.3 | 17323.5 |
| 22 | | | 16029.3 | 802.7 | 16832.0 | | |
| 23 | | | 16130.5 | | | (1409.7) | 17540.2 |
| 24 | | | 16144.0 | 803.1 | 16947.1 | | |
| 25 | | | 16164.2 | | | (1409.9) | 17574.1 |
| 26 | | | 16431.4 | 802.7 | 17234.1 | | |
| 27 | | | 16481.3 | | | (1409.7) | 17891.0 |
| 28 | | | 16520.9 | 802.6 | 17323.5 | | |
| 29 | 15699.2 | 847.6 | 16546.8 | | | | |
| 30 | 15787.2 | 847.3 | 16634.5 | | | | |
| 31 | 15853.1 | 848.1 | 16701.2 | | | | |

TABLE II (Continued).

| No. | A. | $\Delta\nu$ 846.2 | B A + 846.2 | $\Delta\nu$ 803.1 | C A + 1649.3 | $\Delta\nu$ 606.8 | D A + 2256.1 |
|-----|-----------|----------------------|----------------|----------------------|-----------------|----------------------|-----------------|
| 32 | | | 16866.1 | 803.4 | 17669.5 | | |
| 33 | 16298.2 | 847.7 | 17145.9 | | | | |
| 34 | 16334.7 | | | (1651.1) | 17985.8 | | |
| 35 | 16617.8 | | | (1651.2) | 18269.0 | | |
| 36 | | | 17863.9 | | | (1409.6) | 19273.5 |
| 37 | | | 18373.8 | | | (1410.4) | 19784.2 |
| 38 | | | 18474.7 | 802.5 | 19277.2 | | |
| 39 | 18098.7 | | | (1651.7) | 19750.4 | | |
| 40 | 21260.2 M | 846.1 | 22106.3 M | 803.1 | 22909.4 M | 607.0 | 23516.4 M |
| 41 | 21599.5 M | | | (1649.3) | 23248.8 M | 606.8 | 23855.6 M |
| 42 | 21751.9 M | 846.2 | 22598.1 M | 802.7 | 23400.8 M | 606.8 | 24007.6 M |
| 43 | 21783.8 M | | | (1649.2) | 23433.0 M | 606.9 | 24039.9 M |
| 44 | 22163.2 M | | | (1649.2) | 23812.4 M | | |
| 45 | 23013.3 | 846.4 | 23859.7 | 803.3 | 24663.0 | | |
| 46 | 23059.9 M | 846.1 | 23906.0 M | 803.1 | 24709.1 M | 606.8 | 25315.9 M |
| 47 | 23069.2 M | 846.1 | 23915.3 M | 803.2 | 24718.5 M | 606.9 | 25325.4 M |
| 48 | 23477.0 | | | (1649.8) | 25126.8 | | |
| 49 | 24794.8 | 845.8 | 25640.6 | (1650.0) | 26444.8 | 607.2 | 27052.0 |
| 50 | | | | | 26486.7 | 606.2 | 27092.9 |
| 51 | 25675.3 | 846.8 | 26522.1 | (1649.9) | 27325.2 | | |
| 52 | | | | | 27448.2 | 606.8 | 28055.0 |
| 53 | 25864.2 | 846.6 | 26710.8 | (1649.3) | 27513.5 | 606.9 | 28120.4 |
| 54 | | | | | 27527.2 | 606.7 | 28133.9 |
| 55 | 26077.2 | | | (1649.2) | 27726.4 | | |
| 56 | 27208.3 | 846.7 | 28055.0 | | | (1410.1) | 29465.1 |
| 57 | | | 28063.4 | | | (1410.0) | 29473.4 |
| 58 | 27242.1 | 846.6 | 28088.7 | (1649.7) | 28891.8 | 607.1 | 29498.9 |
| 59 | 27779.2 | 845.9 | 28625.1 | (1649.7) | 29428.9 | | |
| 60 | | | | | 29518.6 | 606.8 | 30125.4 |
| 61 | 27992.3 | | | (1649.8) | 29642.1 | | |
| 62 | 28201.2 | 846.3 | 29047.5 | | | | |

TABLE III. First Spark-Spectrum of Potassium.

| N ^o . | P | $\overline{\Delta\nu}$ 847 | Q = P + 847 | $\overline{\Delta\nu}$ 848 | R = P + 1695 | $\overline{\Delta\nu}$ 847 | S = P + 2542 |
|------------------|---------|-------------------------------|----------------|-------------------------------|-----------------|-------------------------------|-----------------|
| 1 | ± 15165 | ± 844 | 16009 | | | ±(2550) | ± 17715 |
| 2 | 16340 | | | ±(1724) | ± 18064 | | |
| 3 | 18286 | | | (1692) | 19978 | | |
| 4 | 19778 | | | (1682) | 21460 | | |
| 5 | 20230 | 849 | 21079 | | | | |
| 6 | 21758 | 848 | 22606 | 849 | 23455 | 846 | 24301 |
| 7 | 22195 | 847 | 23042 | 846 | 23888 | 849 | 24737 |
| 8 | 22384 | 845 | 23229 | | | (1695) | 24924 |
| 9 | 22444 | | | | | (2549) | 24993 |
| 10 | | | 23337 | 848 | 24185 | 846 | 25031 |
| 11 | | | 23665 | | | (1694) | 25359 |
| 12 | 22909 | 850 | 23759 | 840 | 24599 | 864 | 25463 |
| 13 | 23204 | | | | | 2539 | 25743 |
| 14 | 24102 | | | (1708) | 25810 | | |
| 15 | 24429 | 852 | 25281 | | | | |
| 16 | | | | | 26310 | 847 | 27157 |
| 17 | 24737 | | | (1696) | 26433 | | |
| 18 | 24845 | | | (1701) | 26546 | 847 | 27393 |
| 19 | 24882 | 844 | 25726 | | | | |
| 20 | 24993 | | | (1708) | 26701 | | |
| 21 | 25050 | 844 | 25894 | 850 | 26744 | | |
| 22 | 25171 | | | (1695) | 26866 | | |
| 23 | 25210 | | | (1694) | 26904 | | |
| 24 | 25485 | | | (1707) | 27192 | | |
| 25 | 25779 | 845 | 26624 | 850 | 27474 | 847 | 28321 |
| 26 | 26009 | | | (1696) | 27705 | | |
| 27 | 26187 | | | (1691) | 27878 | 847 | 28725 |
| 28 | | | 27570 | 849 | 28419 | | |
| 29 | 27192 | | | | | (2540) | 29732 |
| 30 | 27246 | | | | | (2541) | 29787 |
| 31 | 27636 | | | | | (2550) | 30186 |

TABLE III (Continued).

| N ^o . | P | $\overline{\lambda}$ 847 | Q = P + 847 | $\overline{\lambda}$ 848 | R = P + 1695 | $\overline{\lambda}$ 847 | S = P + 2542 |
|------------------|-------|-----------------------------|----------------|-----------------------------|-----------------|-----------------------------|-----------------|
| 32 | 28070 | 850 | 28920 | 850 | 29770 | | |
| 33 | 28458 | | | | | (2552) | 31010 |
| 34 | | | 29539 | 846 | 30385 | 845 | 31230 |
| 35 | 28725 | 848 | 29573 | | | | |
| 36 | 28830 | | | | | (2535) | 31365 |
| 37 | 29123 | | | | | (2547) | 31670 |
| 38 | 29371 | | | (1693) | 31064 | | |
| 39 | 29471 | | | (1690) | 31161 | | |
| 40 | 29638 | | | (1704) | 31342 | | |
| 41 | 29888 | 844 | 30732 | | | | |
| 42 | 30101 | | | | | (2551) | 32652 |
| 43 | 30499 | | | (1703) | 32202 | | |

1 × 847, 2 × 848, 3 × 847. From this ensues that Table III is not unequivocally determined, like II, because when e.g. only P and Q occur in a row, they can now equally well be placed in another row in the Q and R or R and S columns.

It makes the impression that the number 847 = D has a physical meaning, as also a value 846,2 occurs in the argon spectrum, which may possibly be a more accurate value for D .

One more detail of the experiments deserves to be mentioned. In some cases the argon spectrum was observed in the potassium tube at the same time with the first spark spectrum of potassium. We have not to do here with a case of transmutation of potassium into argon, but with the penetration of atmospheric air, of which the argon has been finally left. When, however, all precautions are taken, the spark spectrum of potassium is emitted without argon lines.

Mathematics. — “*Explanation of some Interference-Curves of Uni-axial and Bi-axial Crystals by Superposition of Elliptic Pencils.*” (Third paper.) By J. W. N. LE HEUX. (Communicated by Prof. HENDRIK DE VRIES.)

(Communicated at the meeting of March 25, 1922)

Some well-known interference-curves, *i. e.* the hyperbola's and the lemniscates are obtained by superposition of two equal unissons, under certain conditions, as was remarked in my first paper¹).

From this observation we may derive a parameter-equation for both cases, which enables us to construct the curves in a simple manner.

The axes being at right angles, the unisson may be given by

$$\begin{aligned} x &= r \cos 2 \varphi \\ y &= r \cos 2 (\varphi + a). \end{aligned}$$

Each value of the phase-difference $2a$ corresponds to an ellipse; when we suppose, that this phase-difference increases each time with $2a = \frac{\pi}{2n}$, the unisson has n ellipses.

With regard to an easy construction, the angle 2φ may also be supposed to increase with $\frac{\pi}{2n}$.

The two equal unissons, partially covering each other, are given by :

$$\begin{aligned} x &= r \cos 2 \varphi + a \\ y &= r \cos 2 (\varphi + a) + a \end{aligned} \quad \left\{ \begin{array}{l} \dots \dots \dots (I) \end{array} \right.$$

$$\begin{aligned} x &= r \cos 2 \varphi' - a \\ y &= r \cos 2 (\varphi' + a) - a \end{aligned} \quad \left\{ \begin{array}{l} \dots \dots \dots (II) \end{array} \right.$$

where a is constant and $< r$.

The distance between the centres is $2a\sqrt{2}$.

By altering $2a$ (and also $2a'$) from 0 to $\frac{\pi}{2}$, the image of the hyperbola's is obtained, and from $\frac{\pi}{2}$ to π , that of the lemniscates.

¹) These Proceedings Vol. XXIII, p. 1223—1225.

Each curve of the moiré-image corresponds to a certain constant difference (or sum) of phase.

The equation will first be derived for a constant difference of phase $2\alpha - 2\alpha' = 2\theta$.

This condition, together with (I) and (II) gives:

$$\left. \begin{aligned} \frac{x-a}{r} &= \cos 2\varphi \\ \frac{x+a}{r} &= \cos 2\varphi' \end{aligned} \right\} \dots \dots \dots (III)$$

$$\left. \begin{aligned} \frac{y-a}{r} &= \cos 2\varphi \cos 2\alpha - \sin 2\varphi \sin 2\alpha \\ \frac{y+a}{r} &= \cos 2(\varphi'-\theta) \cos 2\alpha - \sin 2(\varphi'-\theta) \sin 2\alpha \end{aligned} \right\} \dots \dots (IV)$$

Eliminating 2α from (IV) by means of the relation

$$\sin^2 2\alpha + \cos^2 2\alpha = 1$$

we get:

$$\left| \begin{array}{c} \frac{y-a}{r} - \sin 2\varphi \\ \frac{y+a}{r} - \sin 2(\varphi'-\theta) \end{array} \right|^2 + \left| \begin{array}{c} \cos 2\varphi \frac{y-a}{r} \\ \cos 2(\varphi'-\theta) \frac{y+a}{r} \end{array} \right|^2 = \left| \begin{array}{c} \cos 2\varphi - \sin 2\varphi \\ \cos 2(\varphi'-\theta) - \sin 2(\varphi'-\theta) \end{array} \right|^2$$

or after reduction:

$$\cos^2 \{2(\varphi-\varphi') + 2\theta\} - 2 \frac{y^2 - a^2}{r^2} \cos \{2(\varphi-\varphi') + 2\theta\} + 2 \frac{y^2 + a^2}{r^2} - 1 = 0 \quad (V)$$

When in this equation $\cos \varphi$ and $\cos \varphi'$ are replaced, resp. by $\frac{x-a}{r}$ and $\frac{x+a}{r}$, we get the equation of the moiré-image in xy coordinates.

It is, however, preferable to seek parameter equations.

Suppose $2(\varphi-\varphi') + 2\theta = 2\Delta$, then (V) becomes:

$$r^2 \cos^2 2\Delta - 2(y^2 - a^2) \cos 2\Delta + 2(y^2 + a^2) - r^2 = 0 \quad (VI)$$

which gives for y :

$$y = \pm \sqrt{r^2 \cos^2 \Delta - a^2 \cotg^2 \Delta} \quad \dots \dots (VII)$$

The value of x follows from:

$$\begin{aligned} 2(\varphi-\varphi') + 2\theta &= 2\Delta \\ \cos 2\varphi \cos 2\varphi' + \sin 2\varphi \sin 2\varphi' &= \cos 2(\Delta-\theta) \end{aligned}$$

or, with regard to (III) and after reduction:

$$r^2 \cos^2 2(\Delta-\theta) - 2(x^2 - a^2) \cos 2(\Delta-\theta) + 2(x^2 + a^2) - r^2 = 0.$$

This equation, being of the same form as (VI), we get for x :

$$x = \pm \sqrt{r^2 \cos^2 (\Delta-\theta) - a^2 \cotg^2 (\Delta-\theta)}.$$

When the original angles φ , φ' , α and α' are again introduced, the parameter equations become:

$$\begin{aligned} x &= \pm \sqrt{r^2 \cos^2 (\varphi - \varphi') - a^2 \cot^2 \varphi} \\ y &= \pm \sqrt{r^2 \cos^2 \{(\varphi - \varphi') + (\alpha - \alpha')\} - a^2 \cot^2 \{(\varphi - \varphi') + (\alpha - \alpha')\}} \end{aligned} \quad \left\{ \begin{array}{l} \text{(VIII)} \\ \text{(VIII)} \end{array} \right.$$

For a constant sum of phase, we find the same equations by changing φ' and α' into $-\varphi'$ and $-\alpha'$.

In both cases, the image is the reflexion of the part in the first quadrant with regard to the axes.

Characteristic is the function

$$f(\varphi) = \sqrt{r^2 \cos^2 \varphi - a^2 \cot^2 \varphi}.$$

which is real for $\sin \varphi > \frac{a}{r}$.

It has an initial value 0 for $\varphi = \operatorname{arcsin} \frac{a}{r}$, a fast reached maximum for $\sin^2 \varphi = \frac{a}{r}$ and it becomes for this maximum $= r - a$.

This is in accordance to the fact, that the circumscribed squares of the partially covering unissons have a common square with sides $= 2(r - a)$, in which square the moiré-image is inscribed.

For the more general case:

$$\begin{aligned} x &= r_1 \cos 2\varphi + b & x &= r_1 \cos 2\varphi' - b \\ y &= r_2 \cos 2(\varphi + \alpha) + a & y &= r_2 \cos 2(\varphi' + \alpha') - a \end{aligned}$$

we find:

$$\begin{aligned} x &= \pm \sqrt{r_1^2 \cos^2 (\varphi - \varphi') - b^2 \cot^2 (\varphi - \varphi')} \\ y &= \pm \sqrt{r_2^2 \cos^2 \{(\varphi - \varphi') + (\alpha - \alpha')\} - a^2 \cot^2 \{(\varphi - \varphi') + (\alpha - \alpha')\}} \end{aligned}$$

Construction of the Hyperbola's.

The construction is similar to that, used for a LISSAJOUS-CURVE, that is: straight lines are drawn parallel to the scaled axes of an orthogonal system and the points of intersection are joined diagonally.

Fig. 1 shows a diagram of the function

$$f(\varphi) = \sqrt{r^2 \cos^2 \varphi - a^2 \cot^2 \varphi}$$

for $a = 8$, $r = 30$. φ is given in units of $\frac{30}{8} = 3\frac{3}{4}^\circ$ and so, the unisson has $\frac{30}{8} = 12$ ellipses.

The maximum ordinate is $r - a = 22$; for $\varphi = \pm 30^\circ$

$$(f(30^\circ) = \sqrt{483} \text{ while } 22^2 = 484).$$

The initial value of $\varphi = 15^\circ$, $\frac{a}{r}$ being $= \pm \frac{1}{4}$.

Between the initial and the maximum value of φ , there are but three ordinates and so, the scaled axes have three dividing-points and the image has three interference-curves, each consisting of four equal parts (Fig. 2).

In the formula, $\varphi - \varphi'$ increases from 15° to 30° and the phase-difference $a - a'$ from -15° to $+15^\circ$.

The constructed curves may be compared to the experimental curves in fig. 3, obtained by superposition of two equal unissons,

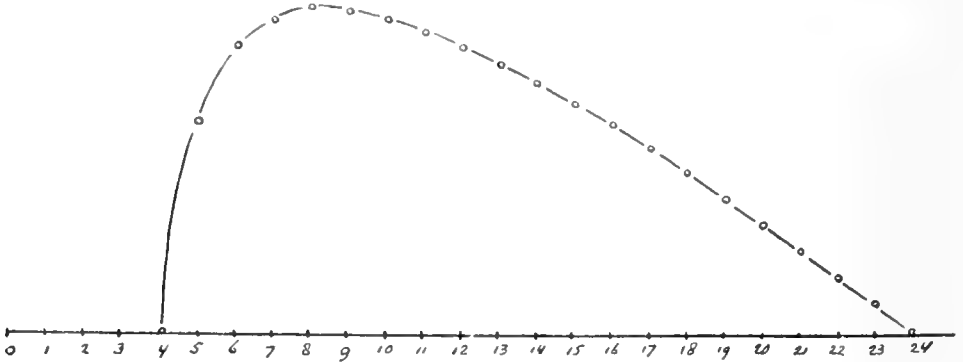


Fig. 1.

each containing 12 ellipses. A much finer result is obtained with unissons of f.i. 50 ellipses, or by comparing to constructed unissons in superposition — these drawings, however, require much time.

It will be evident, that an image with more interference-curves may be obtained by interpolating a *same* number of curves between two succeeding curves of fig. 2.

Construction of the Lemniscates.

This construction is more difficult than that of the hyperbola's, because the image, going to the centre, shows three different species of curves, viz.: ovals, flattened ovals and hyperbola's with doubled ovals.

Only the outer curves are seen in the case of few isophasic lines; they are as easily to construct as the hyperbola's, viz.: by joining the points of intersection, but now following the other diagonal (fig. 4), according to a phase-difference, that begins with 90° .

The constructed curves of fig. 4 may be compared to the experimental curves of fig. 5, the unissons having 12 ellipses each. Fig. 5 is somewhat irregular, owing to the small number of ellipses.

A new difficulty arises from observing, that the axes of co-ordinates are not axes of symmetry for the image of the lemniscates, as is required in the found formula. Still, this image was built in

some experiments, while another time, under apparently the same conditions, a family of ovals appeared. At last, it was found, that the angle between the planes of the pendulums caused the difference: the image of the lemniscates is not built, unless this angle differs from 90° and with a very large number of ellipses per unisson. So in fig. 6, where the angle between the directions of the two composing movements is $\pm 145^\circ$ and each unisson has ± 120 ellipses.

The reason for this large number of ellipses proceeds from the swift rising of the function in fig. 1. Dividing-points near the centre are not obtained, unless the interval 4—5 is divided into f. i. 15 parts, corresponding to a phase-difference of $\frac{1}{4}^\circ = 15'$ and a number of 180 ellipses per unisson.

The experimental number however is limited in consequence of the thickness of the ink-lines.

The phaenomenon is mathematically explained as follows:

The unisson

$$\begin{aligned}x'' &= r \cos 2q, \\y'' &= r \cos 2(q + a)\end{aligned}$$

upon a system with angle 2β , becomes upon an orthogonal system with the same bisectrix:

$$\left. \begin{aligned}x' &= r \sin(\beta + 45^\circ) \cos 2q + r \cos(\beta + 45^\circ) \cos 2(q + a) \\y' &= r \cos(\beta + 45^\circ) \cos 2q + r \sin(\beta + 45^\circ) \cos 2(q + a)\end{aligned} \right\} \cdot (IX)$$

When $\beta + 45^\circ = \gamma$ and seeking the equations of the moiré-image in a similiar manner as before, the composing (oblique) unissons are:

$$\begin{aligned}x &= r \sin \gamma \cos 2q + r \cos \gamma \cos 2(q + a) + a \\y &= r \cos \gamma \cos 2q + r \sin \gamma \cos 2(q + a) + a\end{aligned}$$

and

$$\begin{aligned}x &= r \sin \gamma \cos 2q' + r \cos \gamma \cos 2(q' + a) - a \\y &= r \cos \gamma \cos 2q' + r \sin \gamma \cos 2(q' + a) - a\end{aligned}$$

and a point of the moiré-image has the parameter-equations:

$$\begin{aligned}\frac{x \sin \gamma - y \cos \gamma}{\cos \gamma - \sin \gamma} &= \pm \sqrt{r^2 (1 + \sin 2\gamma) \cos^2 (q - q') - a^2 \cot^2 \gamma (q - q')} \\ \frac{x \cos \gamma - y \sin \gamma}{\cos \gamma - \sin \gamma} &= \\ &= \pm \sqrt{r^2 (1 + \sin 2\gamma) \cos^2 \{ (q - q') + (a - a') \} - a^2 \cot^2 \gamma \{ (q - q') + (a - a') \}}\end{aligned}$$

Now

$$\begin{aligned}\bar{x} &= \pm \sqrt{r_1^2 \cos^2 (q - q') - a^2 \cot^2 \gamma (q - q')} \\ \bar{y} &= \pm \sqrt{r_1^2 \cos^2 \{ (q - q') + (a - a') \} - a^2 \cot^2 \gamma \{ (q - q') + (a - a') \}}\end{aligned}$$

where

$$r_1 = r \sqrt{2} \cdot \sin(\gamma + 45^\circ)$$

is a moiré-image of two orthogonal unissons.

The constant factor $\cos \gamma - \sin \gamma$ only alters the magnitude. When

$$\begin{aligned} x \sin \gamma - y \cos \gamma &= x \\ x \cos \gamma - y \sin \gamma &= y \end{aligned}$$

it follows, that

$$\begin{aligned} x &= \frac{y \cos \gamma - \bar{x} \sin \gamma}{\cos 2\gamma} = \frac{\sin \gamma}{\cos 2\gamma} \cdot (y \cot \gamma - \bar{x}) \\ y &= \frac{\bar{y} \sin \gamma - \bar{x} \cos \gamma}{\cos 2\gamma} = \frac{\sin \gamma}{\cos 2\gamma} \cdot (\bar{y} - \bar{x} \cot \gamma) \end{aligned}$$

Omitting the constant factor $\frac{\sin \gamma}{\cos 2\gamma}$, that does not alter the form, we find at last, that the moiré-image for oblique unissons proceeds from that for orthogonal unissons by the linear substitution

$$\begin{aligned} x_1 &= -\bar{x} + \bar{y} \cot \gamma \\ y_1 &= \bar{y} - \bar{x} \cot \gamma. \end{aligned}$$

The form, thus chosen, gives rise to an easy construction, executed in fig. 7. The new ordinate, f. i. is found by drawing

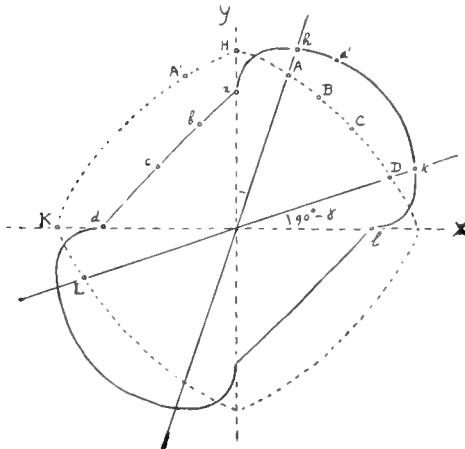


Fig. 7.

the axes, the hyperbola's²⁾ are built.

¹⁾ See the experimental curves in my first paper, fig. 4.

²⁾ A mathematical explanation of interference-curves, wholly different from the here given, is to be found in Mr. T. K. CHINMAYANANDAM: On Haidinger's Rings in Mica. Proc. Royal Society. Vol. XCV, p. 176--189.

The author maintains the pure hyperbola's and the ovals of Cassini, which, however, build a rather rough approximation.

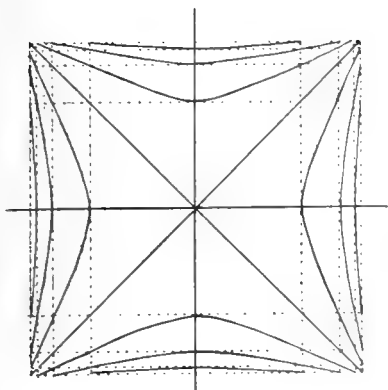


Fig. 2.

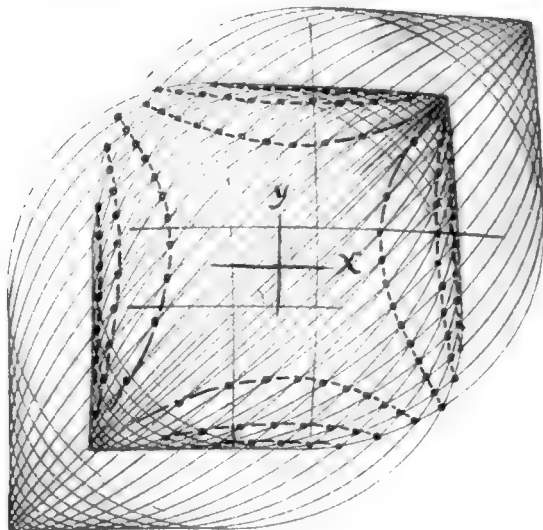


Fig. 3.

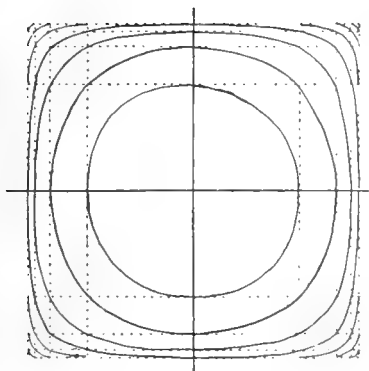


Fig. 4.

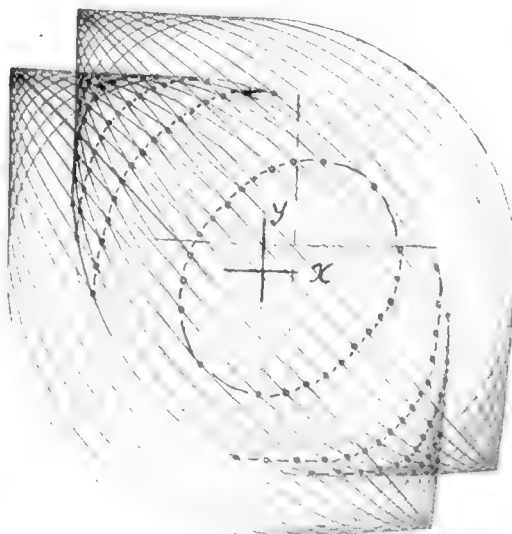


Fig. 5.

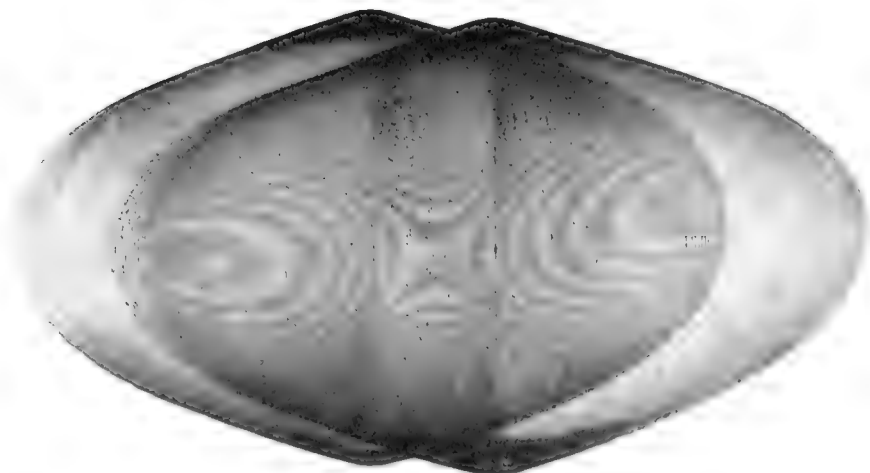


Fig. 6.



Bacteriology. — “*Studies on the bacteriophagus of D’HERELLE.*” II.
By J. W. JANZEN and L. K. WOLFF. (Communicated by
Prof. C. EYKMAN).

(Communicated at the meeting of March 25, 1922).

II. *The Bacteriophagus with regard to flagellates.*

We have been informed by D’HERELLE that the water of some Indian rivers possess the bacteriophagus properties.

In connection with that we have considered it of importance to see how far flagellates out of a mixture of bacteria and bacteriophagus also eat the latter.

In order to do this we prepared a suspension of dead typhoid bacilli in salt solution, and to a third part of this we added 2 cM³ canalwater; a second portion was mixed with bacteriophagus and 2 cM³ canalwater; a third portion was only mixed with the same quantity bacteriophagus as the second.

After 9 days the two first portions had become considerably clearer and we could distinctly show flagellates in the microscopic preparation.

Now dilutions were made, the number of bacteriophagus germs of which was stated in the wellknown way.

We found:

II emulsion + canalwater + bacteriophagus in
1/400.000 cM³ 71 islands.

III emulsion + bacteriophagus in 1/400.000 cM³ 380 islands.

With another trial we found after 14 days:

II emulsion + canalwater + bacteriophagus in
1/4000 mill. cM³ 120 islands.

III emulsion + bacteriophagus in 1/400 mill. cM³ 50 islands.

This numbers are of the same range; the differences range within the mistakes of the experiments.

The suspensions without canalwater remained absolutely turbid, because the bacteriophagus does not affect dead bacilli.

From these two experiments we wish to conclude that the bacteriophagus is not being affected by flagellates.

III. *Constancy of the bacteriophagus properties.*

In our first communication we have proved that various bacteriophagus strains behave differently with regard to different typhoid bacilli.

Here follows a comparison of the bacteriophagus Sm in the sixth and tenth generation with regard to four different typhoid strains; the bacteriophagus was always fed with typhoid Sm.

| | 1. Clearing. | | | 2. Checking. | | | 3. Islandformation. | | |
|---------|----------------|------|------|-----------------|------|------|---------------------|------|------|
| | 6th generation | | | 10th generation | | | | | |
| Strains | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Wi | — | ++ | — | — | ++ | — | — | ++ | — |
| 23 | ++ | ++ | +++ | ++ | ++ | +++ | ++ | ++ | +++ |
| 24 | — | — | — | — | — | — | — | — | — |
| 25 | ++++ | ++++ | ++++ | ++++ | ++++ | ++++ | ++++ | ++++ | ++++ |

So here we see an absolute conformity.

The behaviour of bacteriophagus Sm with regard to strain Wi is somewhat strange; in some generations we did not find any effect; in some others as above mentioned we did find shecking of the growth in broth, but no islandformation.

We have now observed whether the properties of the bacteriophagus change when it is cultivated on different bacteriastrains.

In the following tables the results are given in which

- I. Bacteriophagus Re direct from faeces,
- II. „ „ Re after having been fed with typhoidbacilli Sm,
- III. „ „ Wi direct from faeces,
- IV. „ „ Wi after having been fed with typhoidbacilli Wi,
- V. „ „ Wi after having been fed with typhoidbacilli Sm,
- VI. „ „ Sm after having been fed with typhoidbacilli Sm.

The thus obtained bacteriophagi were examined with regard to 5 typhoidstrains.

From this we see that the properties of the bacteriophagus do change when another bacillus has served as food in this sense, that no bacilli which used to affect are now left uninfluenced, but that an increase can appear in the number of strains which are influenced by the bacteriophagus; except for this strengthening however the bacteriophagus retains its specific properties, which in our opinion pleads more for a living being than for a ferment.

1. Clearing.

2. Checking.

3. Islandformation.

| I Bact. Re direct from faeces. | | | | II Bact. Re after having been fed with typhoidbacilli Sm. | | |
|--|------|------|------|---|------|------|
| Typhoid strains | 1 | 2 | 3 | 1 | 2 | 3 |
| Wi | — | — | — | — | — | — |
| 1 | — | +++ | +++ | — | ++++ | ++++ |
| 24 | — | — | — | — | ± | ++++ |
| 27 | — | — | — | — | — | — |
| 29 | — | — | — | ++ | +++ | ++++ |
| III Bact. Wi. direct from faeces. | | | | IV Bact. Wi after having been fed with typhoidbacilli Wi. | | |
| Typhoid strains | 1 | 2 | 3 | 1 | 2 | 3 |
| Wi | ++++ | ++++ | ++++ | ++++ | ++++ | ++++ |
| 1 | — | — | — | — | — | — |
| 24 | — | ++ | ++++ | — | ++ | ++++ |
| 27 | — | ± | ++++ | — | ± | ++++ |
| 29 | — | ++++ | ++++ | — | ++++ | ++++ |
| V Bact. Wi after having been fed with typhoidbacilli Sm. | | | | VI Bact. Sm after having been fed with typhoidbacilli Sm. | | |
| Typhoid strains | 1 | 2 | 3 | 1 | 2 | 3 |
| Wi | ++++ | ++++ | ++++ | — | — | — |
| 1 | ++++ | ++++ | ++++ | — | +++ | ++++ |
| 24 | — | +++ | ++++ | — | — | — |
| 27 | — | ± | ++++ | — | — | — |
| 29 | ++ | +++ | ++++ | — | — | — |

*Lab. for hyg. of the University.**Amsterdam, March 1922.*

Physics. — G. HERTZ. “*On the Mean Free Path of Slow Electrons in Neon and Argon.*” (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of March 25, 1922).

The reason for undertaking these measurements was given by researches concerning the efficiency of non-elastic impacts of electrons in neon and argon at potentials just above the excitation-potential. It is known, that those collisions between electrons and the atoms of rare gases, which take place below the excitation-potential characteristic for each gas follow the laws of elastic collisions. As soon as the kinetic energy of an electron surpasses the value corresponding to the excitation potential, it can, on collision with an atom, transfer energy to the latter and thereby raise it from its normal state to a higher quantum-state. This, however, does not take place at every collision between a sufficiently fast electron and an atom; only a certain part, in the case of rare gases most probably only a small fraction, of these collisions is non-elastic and causes excitation of the colliding atom. This fraction we call the efficiency of the particular non-elastic impact. It is equal to the probability that an impact of an electron possessing the required energy really leads to a transfer of energy. It is naturally a function of the velocity of the electron. The form of this function however is not yet known.

In a glow-discharge the two rare gases neon and argon show a characteristically different behaviour, which among other things manifests itself under similar circumstances by producing in neon a much more intensive emission of light than in argon. The reason for this different behaviour according to G. HOLST and E. OOSTERHUIS¹⁾ probably lies in the fact, that in argon electrons having a velocity above the excitation-potential readily transfer their kinetic energy to the argon-atoms thereby exciting the emission of ultraviolet rays (resonance), while in neon only a small fraction of the impacts leads

¹⁾ G. HOLST and G. OOSTERHUIS, *Physica*. **1**, 78, 1921.

to radiation the majority of the electrons only imparting their energy to the neon-atoms after falling through a potential-difference equal to the ionization-potential, thus causing ionization.

In consequence one would expect a great difference in the efficiency of the first non-elastic impact in neon and argon. Preliminary experiments concerning the relative value of the efficiency in these gases however have shown, that this difference is not large enough to explain the different behaviour. So there must be another reason. Beside the excitation-potential and the efficiency there is only one quantity which determines the number of the non-elastic impacts, and that is the mean free path of the electrons. Up to now it was assumed, that the value derived from the kinetic theory of gases for particles of infinitesimal small dimensions and large velocity, viz. $4\sqrt{2}$ times the mean free path of a gas-molecule, should hold for the electrons. Recently however, H. F. MAYER¹⁾ and C. RAMSAUER²⁾ have found, from the measurement of the mean free path of electrons, that also for slow moving electrons this quantity depends on the velocity of the electrons, this dependence being different for different gases. Especially between neon and argon RAMSAUER found a very marked difference. While in neon the mean free path depends only to a slight degree on the velocity of the electrons and is nearly equal to the value of the kinetic theory, argon shows for very slow moving electrons, below 1 volt anomalously large values of the mean free path. The mean free path then decreases and becomes a minimum at approx. 12 volts, the minimum being about one third of the value of the kinetic theory. This fact must be of importance for the phenomena produced by electrons passing through a gas, especially in the case of argon, where the mean free path has its minimum value at a potential nearly equal to the excitation potential.

Considering the great importance of the dependence of the mean free path on the velocity, not only for the understanding of the action of electrons in gases, but also for the theory of the atom, it appeared desirable to me, to verify this dependence by direct experiments, in order to obtain accurate values for the ratio of the mean free paths in neon and argon, this ratio being of importance for the evaluation of comparative measurements in the two gases. The applied method is based on the following idea: If in an apparatus of given geometrical dimensions electrons of a certain velocity are allowed to move in a rare gas in a space, in which there is

¹⁾ H. F. MAYER, Ann. d. Phys. **64**, 451, 1921.

²⁾ C. RAMSAUER, Physik. Zeitschr. **22**, 613, 1921.

no electric field, the mean free path alone will determine their movement and distribution, so long as the velocity of the electrons is not larger than that corresponding to the excitation potential, that is: so long as the impacts are entirely elastic. If the apparatus is then filled successively with different rare gases, the movement of the electrons in the one gas must be the same as that in the other, provided the pressures are chosen in such a way that the mean free path is the same. If, on the contrary, the pressures of both gases has been adjusted so as to make the movement of the electrons the same, the inverse ratio of the corresponding pressures will give the required ratio of the mean free paths under equal pressure. This ratio must be found to be independent of the pressure used in the experiments.

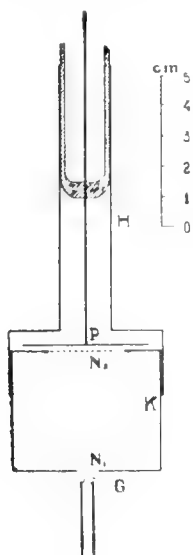


Fig. 1.

The apparatus used is shown in fig. 1. G is a tungsten filament, N_1 and N_2 are grids P is a receiving plate, and H is a metal shield which prevents electrons from coming from G to P by any other way, than through the space between the two grids. All metal parts were made of copper. Before mounting the apparatus they were treated with nitric acid and showed a clean metallic surface after the tube had been exhausted during 5 hours at 400° . The gases used were so pure that no non-elastic impacts, below the excitation potential could be detected even by a very sensitive device.

Before the final measurements, preliminary measurements were made with a simpler device, which differed from that of fig. 1 by omission of the grid N_2 . Though the experiments made in this way do not allow an accurate quantitative evaluation, the results are given here briefly, as they show very simply and clearly the different behaviour of neon and argon. During these preliminary measurements the entire apparatus was at earth-potential, except the filament which was brought at a variable negative potential, so as to produce an accelerating electric field between filament and grid. The electron-current passing on to the receiving plate P was measured by a galvanometer. The measurement consisted simply in noting the current as a function of the accelerating potential between G and N_1 , in neon and argon under various pressures. In order to be independent of slow variations of the current in the filament, a second galvanometer registered the total electron current, and the quotient of the plate-current and the total

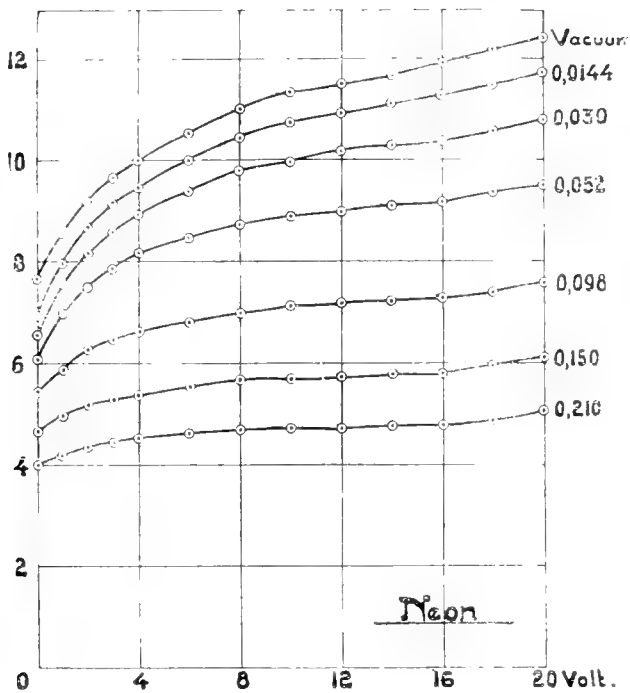


Fig. 2.

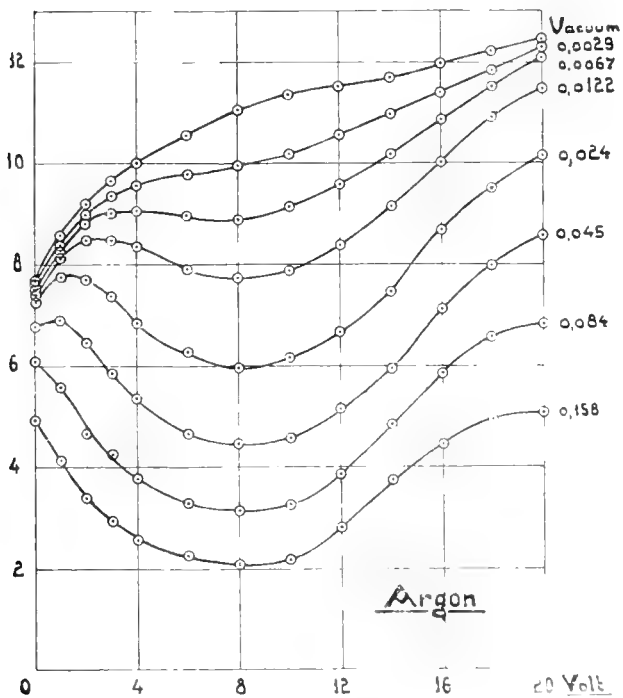


Fig. 3.

electron current from the filament was calculated. As the temperature of the filament was always low, this quotient was independent of the intensity of the electron emission of the filament.

This quotient, multiplied by a constant is plotted in the curves of the figs 2 and 3 for a series of pressures in neon and argon as a function of the potential difference between G and N_1 . The numbers near the curves show the gas pressure in m.m. mercury. We see immediately the extra-ordinary difference in the behaviour of both gases. While in neon an increase of pressure for all velocities reduces the plate-current in about the same degree, argon shows at 10 volts a remarkable decrease of current at pressures, where at 1 volt practically no influence is observed. As the observed decrease of current can result only from the collisions between the electrons and the atoms of the gas, we can deduce from these measurements qualitatively, that the mean free path of electrons in argon varies strongly with the velocity of the electrons, while in neon this is not the case, or at any rate only to a small degree. A quantitative calculation in the sense of the above consideration can only be taken from these measurings for slow electrons up to about 10 volts; at higher velocities the electrons produce secondary electron emission from the metalwalls. To retain these secondary electrons, the second grid N_2 was introduced a retarding potential equal to $\frac{3}{4}$ of the accelerating potential between G and N_1 being applied between N_2 and P . The result of such series of measurements is shown in figs. 4 and 5 wherein the numbers near the curves again show

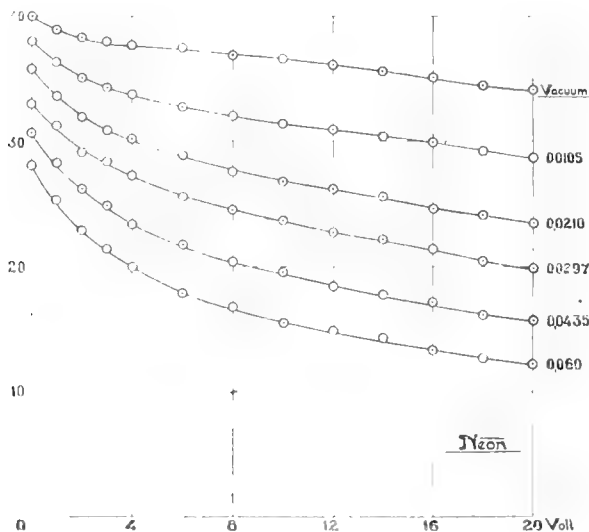


Fig. 4.

the gaspressure in millimetres mercury. For the evaluation of these measurements the distribution of the electron velocities was first measured in vacuo by means of a variable retarding field with the result, that, in consequence of the initial velocity of the electrons, the potential gradient at the filament and the Volta-potential difference

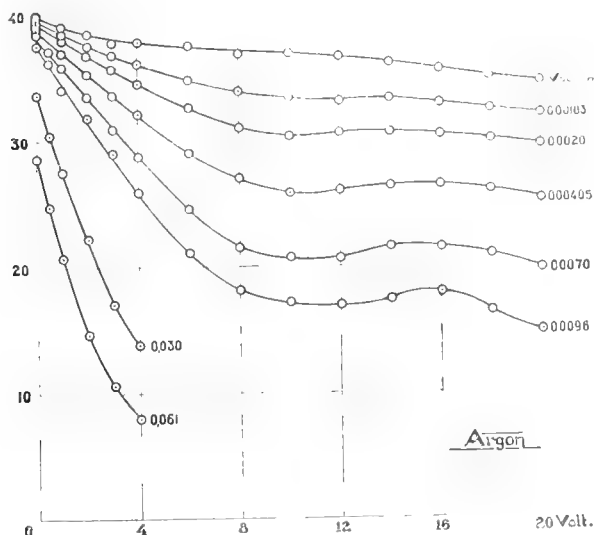


Fig. 5.

between filament and grid, 0.7 volt had to be added to the applied accelerating potential, in order to obtain the true velocity of the electrons. For a series of electron velocities the logarithm of the plate-current was registered as a function of the pressure in neon and argon. A similar character of the curves in neon and argon is to be expected, assuming that the method is correct, in such a way that for each velocity the proportion of corresponding pressures in neon and argon (i.e. pressures giving equal plate-currents) is constant. This is in fact the case for all electron-velocities up to 16 volts. To show this, the curves so obtained for a number of velocities are reproduced in fig. 6. The evaluation is simplified by the fact that the first part of the curves is straight. From the slope of these straight portions we can obtain directly the ratio of the corresponding pressures and so also the ratio of the mean free paths of the electrons.

A condition for the correctness of the method here applied is, that all collisions between electrons and atoms are absolutely elastic. By reason of the very low efficiency of the non-elastic impacts below the ionization potential in the rare gases this is no doubt the case for

potentials between the excitation- and the ionization-potential and for the low pressures used here. Things are different above approx. 16 volts, the ionization potential of argon. This already can be observed at the curves for argon at higher pressures in fig. 5, by a bend in the curves at 16 volts; consequently the ratio of corresponding pressures is no more accurately constant there, as is to be seen in fig. 6 at the curves for 18 volt. At the same time this curve shows,

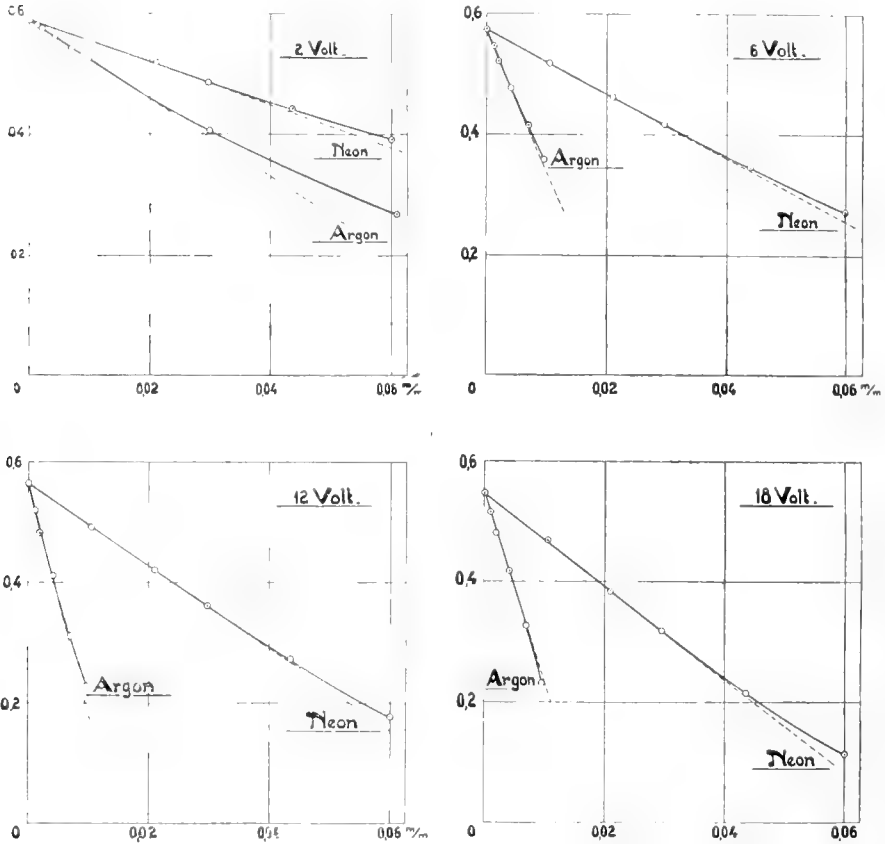


Fig. 6.

that for the lower pressures the number of ionising impacts is so small as to play no part, so that there is no objection against deducing the ratio of the mean free paths from the ratio of the slopes of the first straight parts of the curves.

As a result of the measurement, the values for the ratio of the mean free paths of electrons in neon and argon obtained in this way are shown in fig. 7 as a function of the potential corresponding to the velocity of the electrons; in fig. 8 they are plotted as a function of the root of this potential, being proportional with the

velocity of the electrons. The dotted line in fig. 8 shows for comparison the values of this ratio as deduced from RAMSAUER'S measurements. It will be seen that our measurements verify not only the fact of the variation of the mean free path of the electrons with their velocity, as found by RAMSAUER, but also the general character of this variation. The maximum of the curves was found in the present measurements at a potential about 2 volts less than in RAMSAUER'S.

The action of the slowest electrons is theoretically of special interest. As however the accuracy of such measurements decreases for extremely slow electrons an extrapolation in the direction of the

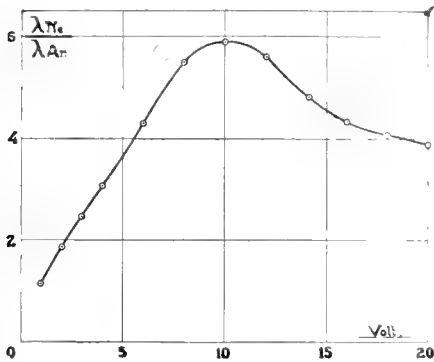


Fig. 7.

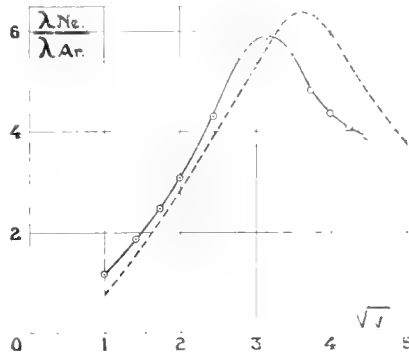


Fig. 8.

velocity zero is always doubtful. If we stipulate, according to the results of RAMSAUER that the electrons in neon show nearly normal values of the mean free path, it appears that, according to the here obtained results, the mean free path of electrons in argon on approaching zero-velocity, do not reach an infinite value, but one about 3 times that calculated from the kinetic theory for very rapidly moving particles of infinitesimal small dimensions. This figure can however, by no means lay claim to accuracy.

The number of collisions of an electron passing through a unit length under the influence of an electric field E , in a gas, in which its mean free path is λ , is $\frac{1}{E} \frac{v^2}{e \lambda^2}$, that is, inversely proportional

of the square of the mean free path. In argon the mean free path, just below 12 volts, the excitation potential, reaches its minimum of about $\frac{1}{3}$ of the value derived from the kinetic theory. We can therefore conclude that an electron of this velocity in argon in passing

through a length unit makes about 9 times as many collisions as would be expected from the kinetic theory, while in neon the number of collisions is nearly normal. This shows clearly, why in argon non-elastic impacts above the excitation potential have a marked effect, while under similar conditions in neon they are hardly noticeable.

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Anatomy. — “*On the morphology of the testis of Rana fusca Rösel*”
By G. J. VAN OORDT. (Communicated by Prof. J. BOEKE.)

(Communicated at the meeting of April 29, 1922.)

Introduction.

In recent years several investigations have given us a better insight into the course and the structure of the seminiferous tubules of a number of Mammals and of one Bird (cock). Formerly it was tried to isolate these tubules by the process of maceration and teasing in order to establish their form, their mutual relation and their connection with the rete testis. The results were not convincing, however, because it could not be traced with certainty whether the free ends found were natural or had originated by tearing.

By means of complete series of sections and wax-reconstructions BREMER (1911) succeeded in disclosing the complicated structure of the embryonic human testis. He discovered that the testis tubules form a closed network. Employing a new, good injection method, followed by maceration and teasing, HUBER and CURTIS (1913) isolated in the testis of the adult rabbit several arch-shaped seminiferous tubules, connected to the rete testis with both extremities. Besides these simple “single-arched” (**n**-like) tubules, “double-arched” (**m**-like) tubules, connected with the three free ends to the rete, were met with. Relatively simple tubules as well as canal-systems of complicated structure were found in the rabbit’s testis; canals terminating in blind ends or diverticula were not described, however. Applying the same method HUBER (1916) discovered in the testis of the cock that the seminiferous tubules form a network, in which no blind ends occur.

Studying complete series of sections CURTIS (1913) met with various single-arched tubules in the testis of the mouse. Anastomoses between two arches occur but rarely. Later on (1918) CURTIS investigated the testes of mouse, rabbit and dog and in these animals he also found the simple **n**-like tubule to be the original one. However, the testis of the mouse shows the simplest structure, then the testis of the dog and next that of the rabbit follows as to complication.

Independent of CURTIS, DE BURLET and DE RUITER (1920) came to the same results in studying a number of complete series of sections

of testes of mouse-embryos of 9—17 mm. length. The fundamental form of the embryonic testis tubule is a simple **n**-like tube, of which the convex side is directed towards the periphery and of which the extremities are connected with the future rete testis. A number of these tubes are placed serially behind each other; anastomoses between the arches and double-arched, **m**-like tubes occur also. The plane of the arch is perpendicular to the longitudinal axis of the testis. Tubules, terminating in blind ends, were rarely found. In the caudal part of the testes of embryos of 13 mm. and smaller a so-called „canal-complex” occurs, from which later on — for in older testes more arches are to be found than in younger ones — additional arches probably develop. The tubules number from 10 to 13 in the mouse. After the „canal-complex” has disappeared, the longitudinal growth of the testis-tubules sets in and then the tubules begin to coil strongly. From the longitudinal stem, originally epithelial, the rete testis develops.

In a second paper DE BURLET (1921) traced the morphology of a few Marsupialian testes (*Perameles obesula*, *Didelphys* spec., *Halmaturus Bennetti*). The single-arched tubule was found again; in *Perameles* the testis (embryo of 50 mm.) is still more simply built than in the mouse; the testis of *Didelphys* (embryo of 20 mm.) is composed of two long, strongly twisted tubules. These tubules are very numerous in *Halmaturus* (embryo of 105 mm.), where they vary from 200 to 300.

Starting from the above investigations it was but natural to trace in one of the representatives of the other Vertebrate groups, how the shape of the adult seminiferous tubule derives from the embryonic one. After consulting Dr. H. M. DE BURLET, to whom I wish to express my thanks for his interest in this work, I chose the common Frog, *Rana fusca* Rösel. As it appeared during the investigation that in immature frogs the course of the vasa efferentia, the ducts through which later on the spermatozoa pass to the kidney, show different peculiarities, I decided to communicate simultaneously a few remarks concerning the course of these channels in immature frogs in the beginning of their second year.

M a t e r i a l a n d m e t h o d s.

All specimens of the common frog were caught at Bilthoven (near Utrecht) in Sept. 1920. The smallest, immature frogs measured 2.8 cm. (from the head to the rump), the largest, adult spec. 6.3 cm. According to GÄUPP (1904, III, pp. 298—300) frogs measuring circ.

30 mm. are in their second, those measuring circ. 50 mm. in their third year, whilst they become mature in the end of the fourth year.

The gonads of the immature frogs were taken from the body, together with the kidney; they were fixed in BOUIN'S solution and after 5 days they were transferred to alc. 90%. Subsequently the testes were cut — mostly frontally, but in a few cases transversely — into complete series of sections of 10 μ . The sections were generally stained with DELAFIELD'S hematoxylin and VAN GIESON'S solution, sometimes eosin or nigrosin was used instead of VAN GIESON'S solution. Especially with VAN GIESON'S solution the connective tissue between the seminiferous tubules assumes a deep red colour.

From the testes of the adult frogs only the middle part was sectioned, from all other testes complete series of sections were made. As far as necessary, the sections were drawn on transparent paper at a magnification of 100, with the aid of the large projection-apparatus of ZEISS.¹⁾ By laying these transparent papers on each other, it is generally not difficult to trace the course of the tubules, which are cut transversely. Originally I had the intention to project on a certain plane several tubules, passing over into the rete testis with a common stem, but in many cases this method proved not practicable, especially in adult testes, as here the tubules are too close to each other and too much twisted. Fig. 10 is even so schematized that only the mutual relations of the tubules, drawn in one plane, are shown. In order to get an exact insight into the course of the seminiferous tubules a few sections of the part of the testis, in which these tubules occur, are also reproduced.

In the following the development and structure of the testis tubules are described in the first place and further the particular course of the vasa efferentia in six immature testes is treated.

The development and structure of the seminiferous tubules.

An extensive literature deals with the development of the gonads of frog-embryos. As most of these investigations do not bear upon my subject, I will only communicate the results of WITTSCH, who in his „Experimentelle Untersuchungen über die Entwicklungsgeschichte der Keimdrüsen von *Rana temporaria*” (1914) not only traced the different developmental stages of the gonad, but also drew attention

¹⁾ I have to thank Prof. A. J. P. VAN DEN BROEK, whose kindness enabled me to use the apparatus of the Anatomical Institution of the University at Utrecht.

to the morphology of the testis tubules of newly metamorphosed frogs.

After describing the development of the so-called indifferent gonad — which possesses a germinal epithelium consisting of one layer

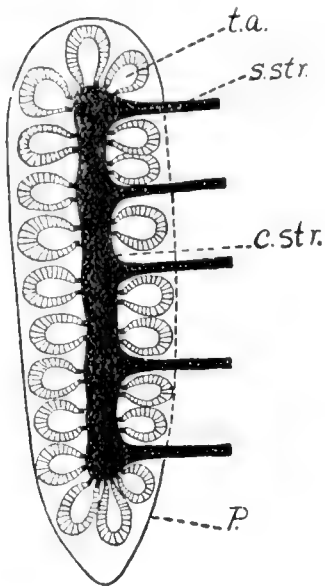


Fig. 1.

Schematized longitudinal section of the testis of a newly metamorphosed frog. After WITSCHI (1914).

and surrounding a central lumen, the primary genital space, in which cell-strands, the sexual strands, situated at regular distances behind each other, have originated from the mesonephros — WITSCHI traces the development of the ovary and the direct testis-development. The indirect testis-development, which takes place in the so-called hermaphrodites of PFLÜGER is elaborately described; in this case the testis originates from an ovarium-like gonad¹). As this development does not bear directly upon my subject and as the final stage of both direct and indirect testis-development is the same, I will not enter any further upon this question. Shortly, the direct testis-development is as follows. The germ cells leave the germinal epithelium, wander through the primary genital space and settle on the sexual strands. All germ cells leave the germinal epithelium about simultaneously, so that only the peritoneum remains. Between the germ cells and the compact core of the sexual strands several slits originate: the anlagen of the lumina of the testis-ampullae. Then the ampullae differentiate from each other and in this way the anlagen of the testis tubules develop. These ampullae are short, almost globular tubules, with a lumen disappearing later on.

The convex side of the ampullae is directed towards the periphery of the testis; with the other side they are attached to the central strand. The sexual strands are connected with the mesonephros. The distal ends of these strands thicken, fuse and in this way the central strand originates in the longitudinal axis of the juvenile testis. After some time the inner-testicular network or rete testis originates from the central strand, as well as the vasa efferentia from the compact sexual strands.

A schematized longitudinal section of the testis of a newly meta-

¹) WITSCHI's latest publication (1921) treats the same subject.

morphosed frog is reproduced in fig. 1, which is drawn after WITSCHI (1914, fig. A, p. 21.)

In the literature, dealing with the further development of the testis, only some scattered remarks on the testis tubules are to be found. "Damit (i.e. when the stage, reproduced in fig. 1 is reached) haben die Samenkanälchen im wesentlichen ihren definitiven Zustand erreicht" (WITSCHI 1914, p. 20). Then the testis ampullae grow out "zu den bekannten schlauchförmigen und gewundenen Samenkanälchen, während sich die Keimzellen ziemlich rasch vermehren" (WITSCHI 1914, p. 20). However, nothing is mentioned about this outgrowth and about the question whether the tubules are connected with each other.

GAUPP describes the form of the testis tubules of the adult frog as follows (1904, III, p. 307): "Sie beginnen an der Oberfläche gerade und mit radiärer Anordnung gegen das Centrum hin, laufen dagegen mehr central vielfach gewunden durch einander. Die radiären Canalabschnitte der peripheren Zone beginnen blind unter der Tunica albuginea, und häufig sieht man hier, wie zwei gesondert entstehende sich mehr central mit einander vereinigen".

It is my intention to trace how the structure of the adult testis originates from the simple one of newly metamorphosed frogs, the latter having been described by WITSCHI.

I started with the study of testes of frogs in the beginning of the second year. It proved easiest to get an insight into the form of the testis tubules by studying frontal testis-sections, in which a great number of transversely cut tubules are visible (cf. figs. 2, 3, 6, 7, 8, 9). These sections were drawn on transparent paper and then compared.

In figg. 2 and 3 parts of two frontal sections of the right testis

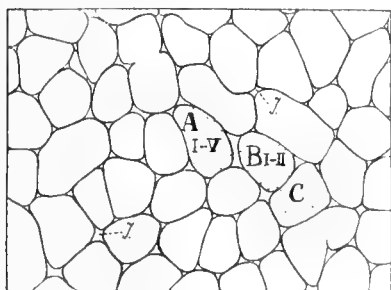


Fig. 2.

Section of the testis of a juvenile frog (beginning of second year), near the rete testis ($\times 100$).

(long 1.8, broad 1 mm.) of a common frog with a head-rump length of 3.5 c.m. are reproduced. Fig. 2 is a section close to the rete: many tubules transversely cut, are distinctly visible. On tracing the course of the three tubules, designated A, B and C, to the periphery, we observe that in most cases these tubules branch, like the fingers of a hand, into a number of tubules (fig. 3, which is drawn after a section close to the periphery) and that all these tubules are

terminating in blind ends. Tubule *A* ramifies into five tubules (*A I*, *A II*...*A V*), *B* into two tubules (*B I*, *B II*), while *C* remains

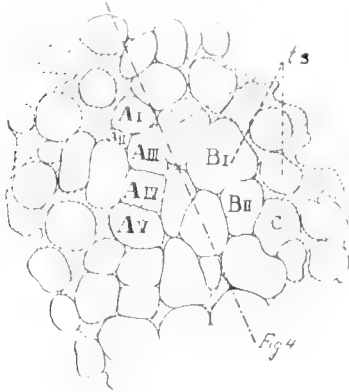


Fig. 3.

Section as in fig. 2, but more near the periphery ($\times 100$).

were indistinctly visible and for this reason this part of the section is shaded by oblique lines.

To elucidate the course of the seminiferous tubules, I have projected the circumferences of the testis tubules *A*, *B* and *C* on a sagittal plane of the testis (this plane is marked by a — . — . — line in fig. 3). This is reproduced in fig. 4, in which the course of these tubules can be seen. Moreover it is visible that the ducts of the rete into which the tubules *A*, *B* and *C* pass over, are directly connected with each other.

The left testis of the same frog was cut transversely. The testis tubules are built in the same manner as those of the right testis. However, on comparing the form of the tubules of the cranial and caudal part of the left testis with the form of the tubules of the middle part of the right testis, we see that in the former the number

of simple, not branching tubules is much larger than in the latter. A peculiarity of this left testis is that the most caudal vas efferens is not connected with the rete testis. In this testis there is a small caudal part, consisting only of three testis tubules, which do not open into the rete, but are directly connected with the mesonephros

single. Already in fig. 2 it is visible that the tubules *A* and *B* divide into a certain number of branches, for these tubules are designated *A I—V* and *B I—II* in this figure. On comparing figs. 2 and 3 we see that the space between the tubules, the interstitium, is larger near to the rete than towards the periphery. As has already been mentioned, fig. 3 is drawn after a section close to the testis-surface, so that not all testis tubules are cut transversely. Many tubules, which were not cross-cut,

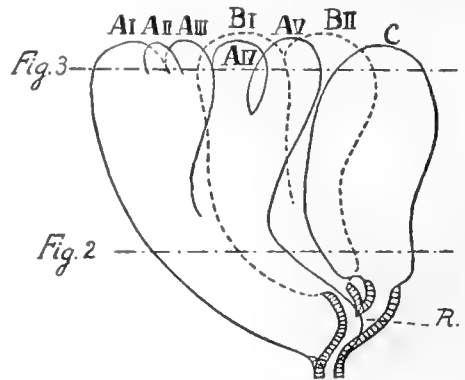


Fig. 4.

Projection of the tubules (designated in figs. 2 and 3) on a sagittal testis-plane ($\times 150$).

by an efferent duct. In fig. 5 this is figured. Only these caudal vasa efferentia are projected on the mid-sagittal plane of the testis. Moreover, two single testis tubules, directly passing over into the rete testis, are sketched; the vas efferens, previous to the last, gives off a side branch to the last efferent duct, but a connection is not established, however.

Two frontal sections of the left testis (long 6, broad 3.5 m.m.) of a frog in the beginning of the third year (4.75 c.m. in length) are reproduced. Fig. 6 shows a section, close to the rete testis, of which different parts are visible. The tubules *A*, *B*, *C* and *D* are separately connected with the rete; tubule *B* just ends in the rete in the section reproduced; in a neighbouring section tubule *C* is connected with this same rete canal. In this figure arrows indicate with which part of the rete a few of the testis tubules are connected.

When we trace the course of the testis tubules, indicated *A*, *B*, *C* and *D* towards the periphery, we see that here also these tubules divide into many others; e.g. tubule *A* splits up into seven, *B* into five, *C* into four and *D* into six others. Fig. 7 shows a section of the same testis about halfway the periphery. At this level tubule *A* has divided into 3 branches (*A I—II*, *A III—V*, *A VI—VII*), *B* into three (*B V*, branched off nearer to the rete is very short), *D* into four, while tubule *C* has not divided as yet; this will take place closer to the periphery. The space between the tubules, being rather wide near the rete, is very narrow at this level. Most tubules end near the periphery; anastomoses are never found.

On comparing the testis of a newly metamorphosed frog (fig. 1) with that of a second or third-year one (figs. 2—7), we find that the testis tubules, which are single originally and terminate in blind ends, divide already in the second year into a number of branches (like the fingers of a hand) and that this subdivision has increased in the

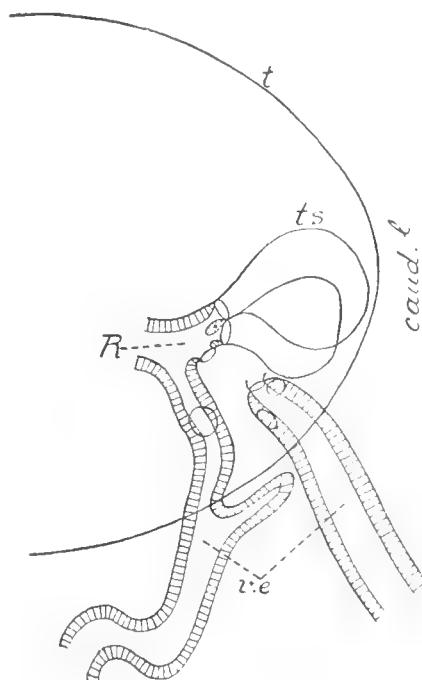


Fig. 5.

Projection of the two posterior vasa efferentia on the sagittal longitudinal testis-plane. Frog from the beginning of the second year ($\times 100$).

third year. The testis having strongly increased in size during this time, it is impossible that several testis-ampullae have fused to form

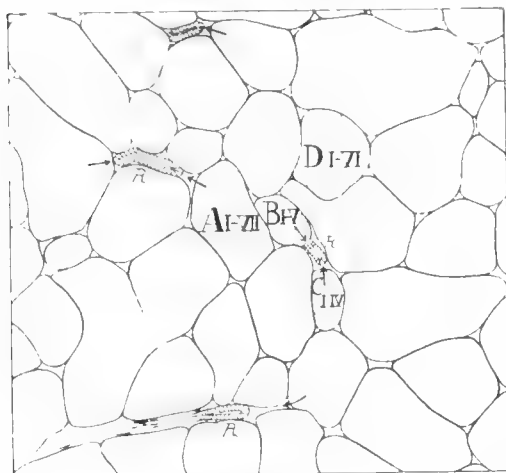


Fig. 6.

Section of the testis of a frog of the third year; the rete is partly visible ($\times 50$).

length and diameter of the seminiferous tubules have strongly increased.

Turning now to the testis of the adult frog, we observe almost the same here. In figs. 8 and 9 parts of two frontal sections of the left testis (long 10.5, broad 7 mm.) of an adult common frog (length 6.3 cm.) are reproduced. The tracing of the course of the strongly ramified testis tubules and the graphic reconstruction of this taking too much time, I can only describe a few tubules, not very strongly branched. They are reproduced in figs. 8 and 9 and a reconstruction of the same tubules, beside each other and in one plane is given in fig. 10. This had to be done, because the tubules, winding too much around each other, especially in the neighbourhood of the rete, could not be reproduced, projected on a certain plane.

The tubules, designated *A I* and *A II* in fig. 8 do not branch

such a canal system. On the contrary, we must conclude from the stages, described above, that the testis tubules, which are originally simple and very short and which are called testis ampullae then, divide toward the periphery into a number of tubules and that these branches are connected with the rete by the proximal part of the ampulla. On comparing the different sections¹⁾ we see that both

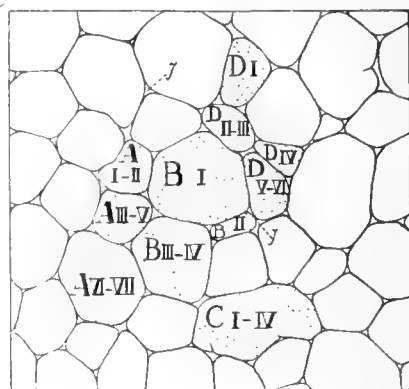


Fig. 7.

Section as in fig. 6, but about half-way the periphery ($\times 50$).

¹⁾ Originally I had the intention to reproduce all the figures at the same magnification ($\times 100$); this proved impossible, however, the figures of immature frog-testes then becoming too small and those of adult frog-testes becoming too large.

further towards the periphery; tubule *B I—II* (fig. 8) splits up into two tubules towards the periphery (fig. 9), while *B III* is very

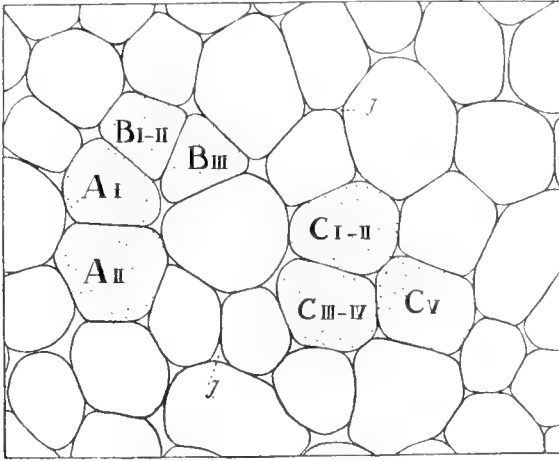


Fig. 8. Section of the testis of an adult frog, about halfway the rete ($\times 50$).

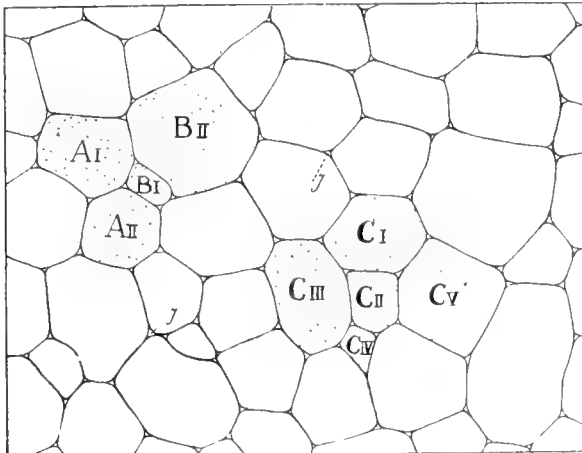


Fig. 9. Section of the testis of an adult frog, near the periphery ($\times 50$).

short and ends blindly about halfway the periphery (fig. 10). If the testis had developed further, this short tubule would probably have grown peripherally. Tubule *C* divides into 5 parts. *A*, *B* and *C* are connected with the rete close to each other.

On comparing this testis with those, described above, we see that apart from the size, there is no fundamental difference in the shape of the tubules. The seminiferous tubules of the adult testis have the same shape, but are longer and thicker. They form no anastomoses and all end blindly. Most of them are strongly branched. The tubules twist, especially near to the rete. Towards the periphery the tubules are situated so close to each other that there is but a

very narrow space left for the interstitium. Towards the rete testis this space increases in width (cf. figs. 9 and 8).

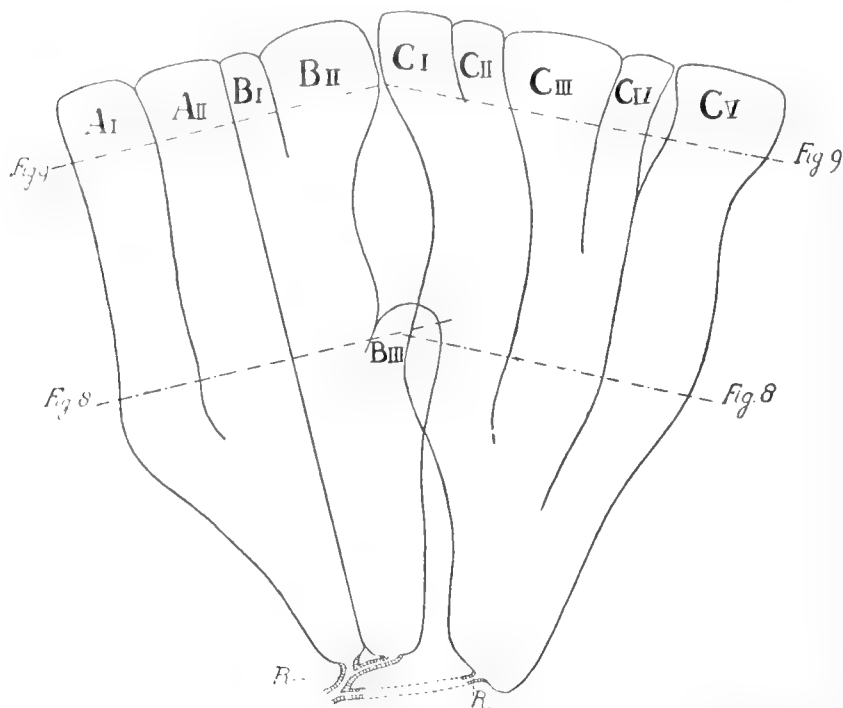


Fig. 10. Schema of the course of the testis-tubules, designated in figs. 8 en 9 ($\times 50$).

The course of the vasa efferentia in frogs in the beginning of the second year.

It is generally known that in adult frogs the vasa efferentia, which arise at the medial side of the testis, form a network, the extratesticular network, between testis and kidney. The number of these channels greatly varies. According to GAUPP (1904, III, p. 355) they number from 4 to 11 in *Rana fusca*. These differences are not only individual, but occur also in the right and left testis of one and the same animal. Channels which terminate blindly and do not reach the kidney are numerous, according to GAUPP.

Investigating a number of testes of immature frogs, I found that here these peculiarities were also present. A conspicuous difference is that the extratesticular network has not developed as well as in adult frogs, the vasa efferentia being still situated serially close behind each other in the mesorchium.

I will describe six testes, derived from two frogs of 2.8 cm. and one frog of 3 cm. in length. With regard to the vasa efferentia,

they show the following peculiarities and differences, sketched schematically in fig. 11 *a—f*; testes, corpora adiposa and kidney are dotted, while rete testis and vasa efferentia are black. For simplicity's sake all the ducts are indicated by successive numbers.

Fig. 11*a* gives a schema of the right testis of a frog, measuring 2.8 cm. in length. From the testis to the mesonephros 4 efferent ducts run, of which the two last have fused over some distance. At the cranial side of the testis there is also a vas efferens (N^o. 2), but this one is not connected with the mesonephros. It runs cranialward and ends in the fat body. Still more in front of the fat body there is a very short vas efferens, connected neither with the testis nor with the kidney.

In fig. 11*b* a schema of the left testis of the same juvenile frog, with 10 efferent ducts is reproduced. The most cranial one, running only over a short distance in the fat body, can be compared to the first vas efferens of the right testis of the same frog. The rete testis is connected by 8 different vasa efferentia (N^{os} 2—9) with the mesonephros. N^{os} 5 and 6 arise from the rete at some distance from each other, but quite near to the testis-surface they come close together and run parallel without fusing, however, to the mesonephros. The two ducts (N^{os} 8 and 9) at the caudal side of the testis arise close to each other but separately, from the testis, and unite just outside the testis to form a common duct. As is the case in the testis described above (p. 8) and sketched in fig. 5, the 10th vas efferens is not connected with the rete testis. Only a few seminiferous tubules open into this duct; so these are directly connected with the kidney.

The two testes sketched in fig. 11*c* and 11*d* belonged to a frog, also measuring 2.8 cm. in length. In both the most cranial efferent ducts have no direct connection with the mesonephros, but run cranialward to the fat-body and from here to the kidney. In the right testis, behind this efferent duct, there are still six others, from which N^{os} 3 and 4 are only separated over a short distance, quite near to the kidney.

In the left testis of the same animal the 2^d and 3^d vasa efferentia arise separately from the rete; they fuse near the mesonephros to form a common duct. The caudal vasa efferentia, N^{os} 5 and 6, run parallel in the testis and unite there, where they leave the testis; then they split, subsequently they again form one duct and finally they enter the kidney separately.

The right testis of the specimen, the last to be described (3 cm. in length), shows only one peculiarity (fig. 11*e*) i.e. the 3rd and 4th

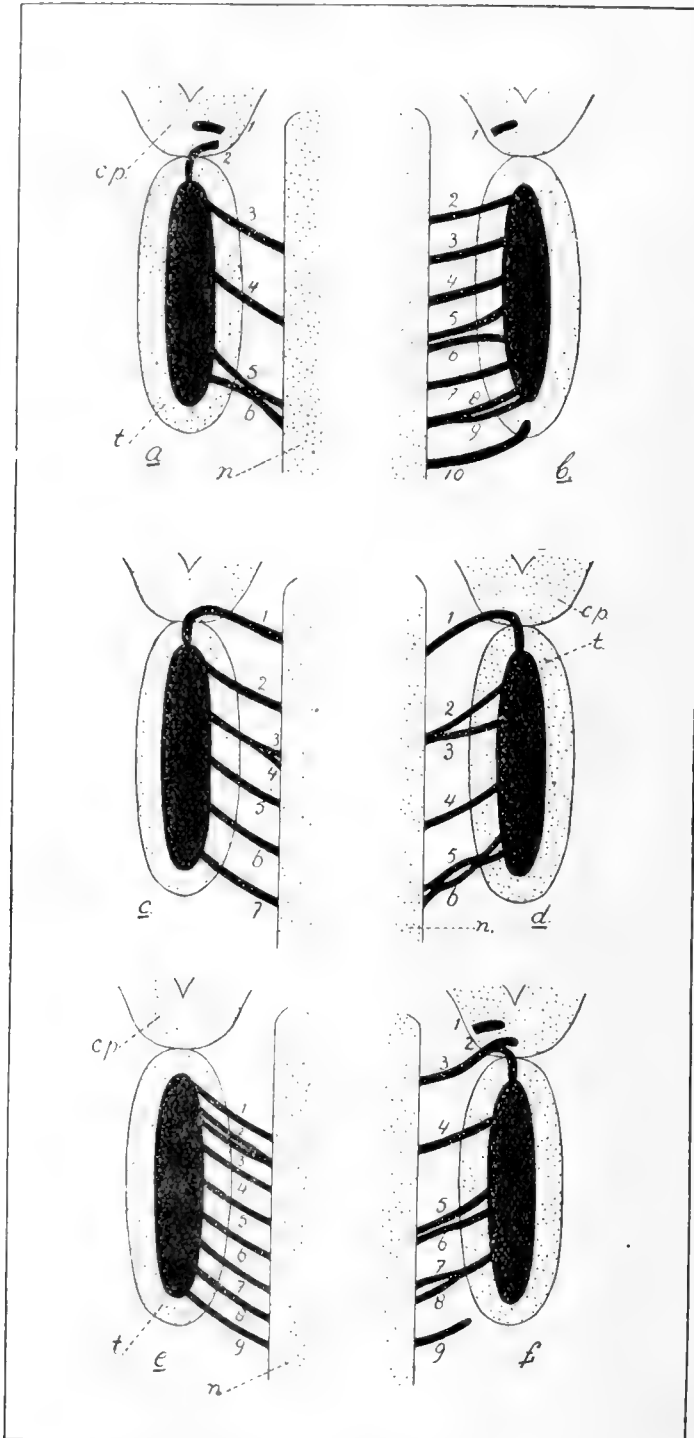


Fig. 11. Schemata of the course of the efferent ducts in 6 testes of juvenile frogs.

vasa efferentia, running close to each other, fuse near the kidney.

The left testis is remarkable for the following facts (fig. 11*f*). The most cranial vas efferens runs like the most cranial ones, sketched in fig. 11*a* and 11*b*; the third vas efferens runs like both cranial efferent ducts of fig. 11*c* and 11*d* and moreover, a short side-duct (N^o. 2), coming from the fatbody, opens into it. The vasa efferentia Nos 5 and 6 are close to each other, especially outside the testis, but enter the mesonephros separately. The 7th and 8th vasa efferentia leave the rete testis united and split outside it; the 9th vas efferens finally is connected with the kidney, but does not reach the testis.

So we have seen that the course of the efferent ducts in immature frogs is as variable as in adult ones and that there is no symmetry between left and right testis of the same animal.

SUMMARY.

I. According to WITSCHI the testis of a newly metamorphosed *Rana fusca* is composed of a great number of short tubules, the testis-ampullae, which end blindly, and are implanted around and perpendicular to a longitudinal stem, the central strand. With this central strand the mesonephros is connected by the sexual strands. The ampullae, which possess a lumen, disappearing later on, form no anastomoses and are not branched. Later on the rete testis originates from the central strand, the vasa efferentia from the sexual strands.

II. During the further development of the testis, the testis-ampullae increase in length as well as in diameter and they simultaneously divide towards the periphery into a great number of branches, which nearly all grow out till they reach the periphery. Only a few short tubules, not reaching the testis-surface, were noted.

III. The testis-tubules of an adult frog, are composed in the same way: towards the periphery they split up more and more. All tubules terminate in blind ends, and they never form anastomoses. The tubules, which are straight near the periphery, are often somewhat bent and twisted near to the rete.

IV. In two testes of immature frogs it was observed that a small caudal part of the testis is not connected with the rete, but that the tubules, composing it, opened directly into an efferent duct.

V. The courses of the vasa efferentia of six immature frogs in the beginning of the second year show several peculiarities:

1. A real network, as in adult frogs, was not noted.

2. In the fat-body short tubules often occur, neither connected with the testis nor with the kidney.

3. In some cases the cranial part of the rete testis is connected with the kidney by an efferent duct, which first passes through the fatbody. In one case a short side-duct, coming from the fatbody, opened into such a duct.

4. It was often observed that vasa efferentia, which run close together, fuse. This fusion can take place near the testis as well as near the kidney.

5. In a few cases an efferent duct was found, which, originating from the mesonephros, did not reach the testis.

6. The vasa efferentia between rete testis and mesonephros number from four to nine, this agreeing with the number, observed in adult frogs. In the left and the right testis of the same animal the number can vary.

Utrecht, April 1922. Zoological Laboratory, Veterinary College.

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ABBREVIATIONS.

c.p. = corpus adiposum, fat body.

c.str. = central strand.

I. = interstitium.

n. = kidney.

P. = peritoneum.

R. = rete testis.

s.str. = sexual strand.

t. = testis.

t.a. = testis-ampulla.

t.s. = tubuli seminiferi, testis tubules.

v.e. = vas efferens.

Mathematics. — “*A New Method for the Solution of the Problem of the Characteristics in the Enumerative Geometry.*” By G. SCHAAKE. (Communicated by Prof. HENDRIK DE VRIES.)

(Communicated at the meeting of April 29, 1922).

§ 1. In this paper a general method will be set forth for the determination of the expressions through which the problem of the characteristics in the enumerative geometry is solved. These are the expressions indicating how many individuals two algebraical systems resp. of ∞^p en ∞^{n-p} figures, depending on n parameters, have in common.

The method in question will be best explained by application to a special example. We shall therefore by the aid of it solve the problem of the characteristics for the straight line in a space of an arbitrary number of dimensions. ¹⁾

§ 2. We shall first confine ourselves to the straight lines of a plane V . In V we assume a point C and a straight line c by the aid of which we represent the plane homographically on itself. With a view to this we associate to a point P of V the point P' of the straight line CP that together with C , the point of intersection C' of CP and c , and P' forms an anharmonic ratio that is equal to a constant number λ . Through this transformation a straight line l of V is transformed into a straight line l' cutting l on c .

Especially we consider the transformation for which $\lambda = 0$. In this case for an arbitrary point P the distance $C'P' = 0$, so that the point P' corresponding to a point P generally lies in the intersection of CP with c . If, however, P lies in C , together with the straight line CP also the distance $C'P'$ becomes indefinite, so that to the point C all the points of V are associated.

For an arbitrary straight line l the corresponding line l' coincides with c . If, however, l passes through P , there are ∞^1 associated

¹⁾ Cf. for other applications Cap. VI of my academical dissertation which will shortly appear, entitled: *Afbeeldingen van figuren op de punten eener lineaire ruimte*, Groningen, P. NOORDHOFF, 1922.

straight lines, which form a plane pencil that has the intersection of l and c for vertex.

If λ changes continuously, out of a system S of ∞^1 straight lines through the homographic representation described above, ∞^1 new systems are derived forming a coherent set, which contains S (for $\lambda = 1$) and of which we shall especially consider S' , the system arising from S through the transformation belonging to $\lambda = 0$. The number of straight lines which a system of this set has in common with a system of ∞^1 straight lines not belonging to the set, is apparently independent of λ . In order therefore to know how many straight lines S has in common with another system S^1 of ∞^1 straight lines, we may equally well investigate the same for S' .

Now any straight line of S is transformed into the line c , which may always be chosen outside S^1 . If, however, S contains k straight lines l passing through an arbitrary point, so that k is the class of the curve enveloped by the lines l , the k straight lines of S through C are transformed into as many plane pencils of straight lines l' . S^1 contains k^1 lines of each of these plane pencils, if the straight lines of S^1 envelop a curve of the class k^1 . From this we conclude that S' and S^1 , hence also S and S^1 , have kk^1 straight lines in common.

§ 3. In order to apply the same method to the straight lines of space, we assume a point C and a plane γ , and we make use of the homographic representation arising if to each point P we associate the point P' that forms with C , the point of intersection C' of CP with γ , and P an anharmonic ratio $= \lambda$; in this representation there corresponds to any straight line l another straight line l' cutting l on γ . If again we take the case $\lambda = 0$, to any straight line l a straight line l' of γ is associated, the intersection of the plane (C, l) with γ , unless l passes through C in which case there are ∞^2 associated lines l' , which form a sheaf of rays that has the point of intersection of l and γ for vertex.

In this way a ruled surface R is represented in a system R' of ∞^1 rays l' of γ . These envelop a curve of the class q , if q is the order of R . For through a point P of γ there pass those straight lines l' that are the images of the straight lines l of R cutting CP . If now we consider a complex K of the order α , this has in γ ∞^1 rays enveloping a curve of the class α , so that K has αq rays in common with R' .

A line complex of the order α has therefore αq lines in common with a ruled surface of the order q .

Through our transformation a congruence G passes into a system G' that consists first of all the rays of γ , each counted β -fold, if β represents the class of G . For each line l of γ is associated to the β lines l of G lying in the plane CU . Further, if α is the order of G , there are α rays of G which pass through C and are transformed into as many sheaves of rays of G' . Another congruence with the order α' and the class β' has $\alpha\alpha' + \beta\beta'$ rays in common with G' . From this follows the well known theorem of HALPHEN:

Two line congruences (α, β) and (α', β') have $\alpha\alpha' + \beta\beta'$ lines in common.

§ 4. Before we give the general solution of our problem in an R_n , we consider the special case that we have to do with the ∞^0 straight lines of an R_4 . By the aid of a point C and a space F in R_4 , we arrive at the ∞^1 homographic representations that are each characterised by a value of the anharmonic ratio $\lambda = (CU'PP')$ if C' is the point of intersection of CP en F . Again we consider especially the representation belonging to $\lambda = 0$.

If we take a system S_1 of ∞^1 rays, this is transformed by the latter representation into a ruled surface S_1' of the order ϱ lying in F , if ϱ represents the number of straight lines of S_1 cutting a plane. If we consider further a system S_2 of ∞^0 straight lines of which an arbitrary plane pencil contains α , the rays that S_2 has in common with F form a complex of the order α , so that S_2 contains $\varrho\alpha$ rays of S_1' .

A system S_1 of the order ϱ has $\varrho\alpha$ rays in common with a system S_2 of the order α .

A system S_2 of ∞^0 rays is represented on S_2' , a congruence (α, β) of F , if α is the number of rays of S_2 cutting an arbitrary straight line (through C), and β the number of straight lines of S_2 lying in an arbitrary space (through C). A system S_4 has a congruence (φ, ψ) in common with F , if φ and ψ represent the numbers of straight lines of S_4 resp. belonging to a (three-dimensional) sheaf of rays or lying in a plane. S_4 has $\alpha\varphi + \beta\psi$ rays in common with S_2' .

A system S_2 (α, β) has $\alpha\varphi + \beta\psi$ rays in common with a system S_4 (φ, ψ) .

A system S_3 is transformed through our representation into a system S_3' consisting first of a complex of the order r lying in F , if r is the number of rays of S_3 lying in a (three-dimensional) special linear complex. Further, if S_3 contains μ rays through a given point, to each of the μ straight lines l through C there are associated the

∞^3 rays l passing through the point of intersection of l and Γ , so that S_3' contains also μ four-dimensional sheaves of rays. If besides S_3 , we have another system S_3^1 with the characteristic numbers μ_1 and r_1 , this has in Γ a ruled surface of the order r_1 and it contains μ_1 straight lines of each of the four-dimensional sheaves in S_3' . S_3^1 and S_3' have accordingly $\mu\mu_1 + r_1r_1$ rays in common.

Two systems $S_3(\mu, r)$ and $S_3^1(\mu_1, r_1)$ have $\mu\mu_1 + r_1r_1$ rays in common.

§ 5. By means of complete induction the following results may be easily proved, through which the problem of the characteristics is solved for the straight line in R_n .

The characteristic numbers of a system S_p of ∞^p rays in R_n indicate how many straight lines of S_p there are in an $R_{n-\mu+1}$ lying in R_n which cut an $R_{n+\mu-p-2}$ in the aforesaid $R_{n-\mu+1}$ for all values of μ satisfying the inequalities: $\mu > 0$, $n + \mu - p - 2 < n - \mu + 1$ or $\mu < \frac{p+3}{2}$ and $n + \mu - p - 2 > -1$ or $\mu > p - n + 1$.

From this follows that the p -fold number of characteristics for the straight line in R_n , if $p < n$, is equal to $\frac{p+1}{2}$ or $\frac{p}{2} + 1$, according to whether p is odd or even, and for $p \geq n$ equal to $\frac{2(n-1)-p+1}{2}$ or $\frac{2(n-1)-p}{2} + 1$ according to whether p is odd or even. The p -fold number of characteristics is, therefore, equal to the $2(n-1)-p$ -fold number.

The expression indicating how many lines an S_p and an $S_{2(n-1)-p}$ have in common, is a polynome of which all the terms are found by multiplying each time those characteristic numbers of S_p and $S_{2(n-1)-p}$ that belong to conditions which together define a straight line in R_n .

§ 6. It is clear that the indicated method may also be applied to the case when we have to do with figures composed of a definite number of points, straight lines, planes etc. If the parts of these figures are independent of each other, it will often be desirable to transform them by different homographic representations.

The system e.g. of the ∞^n groups of n points (P_1, P_2, \dots, P_n) of a straight line l may in the following way be represented homographically on itself. We assume on l $2n$ arbitrary points $C_1, \dots, C_n, F_1, \dots, F_n$ and associate to a point P_i of a group of n points (n -group) the point P'_i defined by: $(C_i, F_i, P_i, P'_i) = \lambda_i$.

If we take all $\lambda_i = 0$, there belongs to an arbitrary n -group the n -group (I_1, \dots, I_n) ; if, however, a point P_i coincides with C_i , the associated point P'_i , becomes indefinite, so that to an n -group of which the k points $P_{i_1}, P_{i_2}, \dots, P_{i_k}$ coincide resp. with $C_{i_1}, C_{i_2}, \dots, C_{i_k}$ there are associated ∞^k groups that have the $n-k$ points $I_{i_{k+1}}, \dots, I_{i_n}$ in common.

Let us now consider a system S_k of ∞^k n -groups with the $\binom{n}{k}$ characteristic numbers $\alpha_{i_1 i_2 \dots i_k}$, indicating how many groups of the system there are for which the points $P_{i_1}, P_{i_2}, \dots, P_{i_k}$ are defined. Through our representation S_k is transformed into a system S'_k consisting of $\binom{n}{k}$ separate systems of ∞^k groups. Such a system is formed e.g. by the n -groups that have their points $P_{i_{k+1}}, \dots, P_{i_n}$ resp. in $I_{i_{k+1}}, \dots, I_{i_n}$ and of which the remaining points P are indefinite. Each group of this system is associated to the $\alpha_{i_1 i_2 \dots i_k}$ groups of S_k that have their points P_{i_1}, \dots, P_{i_k} in C_{i_1}, \dots, C_{i_k} and is therefore an $\alpha_{i_1 i_2 \dots i_k}$ -fold group of S'_k . If we take another system S_{n-k} of ∞^{n-k} groups, with the characteristic numbers $\beta_{i_1 i_2 \dots i_{n-k}}$ we find from the number of common groups of S'_k and S_{n-k} :

A system $S_k(\alpha_{i_1 \dots i_k})$ of ∞^k n -groups of points has with a system $S_{n-k}(\beta_{i_1 \dots i_{n-k}})$ of ∞^{n-k} n -groups $\sum \alpha_{i_1 \dots i_k} \beta_{i_{k+1} \dots i_n}$ groups in common.

Finally we remark that the expounded method may also be applied to curves, surfaces etc.

Physics. — “*On the diffraction of Röntgen-rays in liquids.*” By Prof. W. H. KEESOM and Prof. J. DE SMEDT. (Communication N°. 10 from the Laboratory of Physics and Physical Chemistry of the Veterinary College). (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated at the meeting of March 25, 1922).

§ 1. *Introduction.* The investigation by means of Röntgen-rays of the structure of substances that are in liquid or solid state at temperatures lower than the ordinary one, seems us to be of extraordinary importance. These substances namely belong to those that possess the most simple chemical structure (in the gaseous state several of them are mon- or diatomic). In most cases their molecules consist of light atoms small number of electrons). Therefore the experimental results obtained with these substances will lead more easily than other ones to conclusions of importance for the structure not only of the crystalline state but also of the molecule and the atom.

We thus gladly followed the invitation of Prof. KAMERLINGH ONNES to make such an investigation on the diatomic elements oxygen, nitrogen, if possible on hydrogen etc. and the monatomic elements as f.i. argon. In the discussion of the scheme for this investigation, for which we made at Leiden some preparatory experiments, the first question was the following: Will liquefied gases also give a diffraction figure when they are crossed by a beam of Röntgen rays as it was the case with the liquids that were investigated by DEBIJE and SCHERRER¹⁾? As some Röntgen-technical difficulties had to be overcome we agreed to continue the preparatory experiments at Utrecht, as far as we should be able to obtain there the liquid gases and work there with them. Some of the results of these experiments will be given in this paper. In these investigations we did not only use liquid oxygen and argon²⁾ but also some substances that are liquid at ordinary temperatures.

§ 2. *The apparatus.* Fig. 1 shows the vacuum glass *g* and fixed

¹⁾ P. DEBIJE and P. SCHERRER, Nachrichten Göttingen 1916.

²⁾ The argon was put at our disposal by N.V. Philips' Gloeilampenfabrieken, for which we wish to express here our thanks

to it the camera *c*, into which the liquid gas is poured and in which it will be radiated by the Röntgen beam which is bounded by the diaphragm *d* of tin (length 34 mm., diameter of the opening 2 mm.)

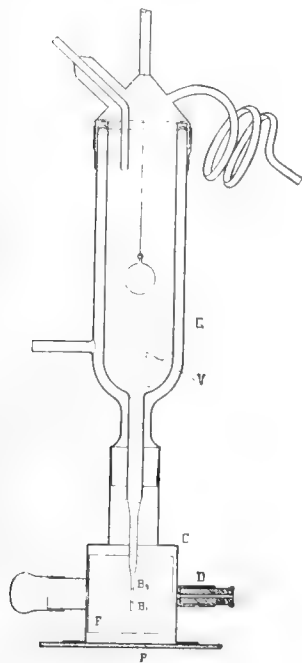


Fig. 1.

shut by a leaf of aluminium. The lower part of the inner tube is narrow. First it consisted of a small tube of aluminium thick 0,015 mm. and with a diameter of 3 mm. which was soldered to a copper tube by means of wolframine. Later on this aluminium tube was replaced by a glass tube thick 0,002^s to 0,01 mm.¹⁾ and with diameter 2 mm., blown to a wider glass tube. Except between *b*₁ and *b*₂ the glass was silvered.

The camera (radius 27,5 mm.) is fixed to the outer glass by means of a ground plug. In the camera along the cylinder wall the film *f*' is stretched (Eastman duplitzed X-ray film) in the same way as was done by DEBIJE and SCHERRER. For taking in and out the film, which was wrapped up in black paper, the camera was detached from the plate *p* to which

its ground border had been cemented. The vacuum was obtained with a LANGMUIR condensation pump with the rotating mercury pump of GAEDE as a forepump. This vacuum sufficed to expose with one single filling of 200 cM³ of the liquefied gas during more than 5 hours.

The Röntgen-rays were excited by a metal SIEGBAHN tube with Cu-anticathode. The *K*_β rays were filtered away by a Ni-plate of 0,01 mm. The current given by an inductorium with gas interruptor was ± 10 mA., tension ± 25 KV., time of exposition as a rule 5 hours.

For a photograph of the Röntgen interference figure of ice (see § 3) we used a glass tube partly filled with water. The lower part of this tube consisted again of a thin glass tube as described above. The tube with water was let down into a vacuum vessel with a lower part of thin-walled glass filled with liquid air. During the exposition the tube was rotated from time to time.

¹⁾ These thin tubes of aluminium and glass are proofs of the ability of the amanuenses 1st class J. J. VAN DER SLUIS and A. R. B. GERRITSE, the last of whom has also made several of the here mentioned photographs.

The substances that are liquid at ordinary temperatures were exposed in a more simple glass apparatus with a thin walled lower part, which fitted on the same camera, while again the camera was evacuated.

§ 3. *Results.* We have exposed liquid oxygen, liquid argon, benzene, water, aethylalcohol, aethylaether, formic acid, carbonic disulphide, bromium.

Of these carbonic disulphide and bromium (in glass tube) gave no distinct diffraction figure ¹⁾.

The other liquids gave first an intense almost circular diffraction ring. Fig. 2 shows the diffraction ring of oxygen.

Argon was exposed twice, once in an aluminium tube and once in a glass tube. Of these only ²⁾ the first one gave a distinct diffraction figure.

In table I φ represents the half top-angle of the cone formed by the diffracted Röntgen rays.

TABLE I.

| Substance | φ | a | $1.33 \sqrt[3]{\frac{M}{d}}$ |
|---------------|-----------|------------------|------------------------------|
| oxygen | 27° | 4.0 Å | 4.0 Å |
| argon | 27 | 4.0 | 4.1 |
| benzene | 18 | 6.0 ³ | 5.9 |
| water | 29 | 3.7 ³ | 3.6 |
| aethylalcohol | 22 | 4.9 | 5.2 |
| aethylaether | 19 | 5.7 | 6.2 |
| formic acid | 24 | 4.5 | 4.5 |

By the agreement between the diffraction rings of oxygen and argon we might come to the hypothesis that these rings are due to the same impurity f.i. to small ice crystals. This was however proved to be not the case. Therefore oxygen namely was first dried by KOH and P₂O₅, then liquefied and distilled in apparatus dried beforehand and finally poured through a filter of cotton wool into

¹⁾ The probable reason for this is, that the Röntgen rays are absorbed to such a high degree by these substances, that the Röntgen-light diffracted by the liquid on account of its small intensity cannot be distinguished from that diffracted by the glass.

²⁾ Probably by the reason mentioned in note 1.

the vacuum glass that was filled with dry air ¹⁾ and in which such a filter was placed again at the entrance of the narrow part. This oxygen now gave the same ring. On the other hand a photograph of ice (see § 2) surrounded by liquid air taught us that none of the interference lines of ice coincide with the ring of oxygen.

The diffraction image of water shows still an interesting detail (see fig. 3 of the plate). Immediately following on the intense diffraction ring the film shows a very considerable almost uniform blackening with a rather sharp outline at $\varphi = 46^\circ$.

For some other liquids too we found weak indications of a similar blackening.

For oxygen and argon the best films show beside the ring given in table I still a weak second ring, for oxygen at $\varphi = 46^\circ$, for argon at $\varphi = 49^\circ$.

§ 4. *The intense diffraction ring is due to the cooperation of neighbouring molecules.* As was shown by EHRENFEST ²⁾ and at the same time by DEBIJE and SCHERRER (l.c.) a diffraction ring like that of § 3 may be due to the interference of Röntgen-rays diffracted by arbitrarily orientated systems each of two (or more) particles, which have a definite mutual distance (f.i. the two atoms in a diatomic molecule, where each of the atoms is regarded as one single diffracting centre.) Between the angle φ and the distance a of the two diffracting particles we have then (see EHRENFEST l.c.) the following relation

$$a = \frac{7,72 \lambda}{4 \pi \sin \frac{\varphi}{2}}, \quad \dots \dots \dots (1)$$

where λ is the wavelength of the Röntgenrays.

The values of a calculated in this way (with $\lambda = 1,54 \text{ \AA}$) are given in table I.

In the first place the fact, that also argon has a similar diffraction ring, involves that, at least for argon, this diffraction ring is not due to the cooperation of atoms in the molecule. ³⁾

That this is neither the case for oxygen is to be expected by the

¹⁾ By a small window v in the vacuumglass we could state that the liquid was perfectly clear.

²⁾ P. EHRENFEST. These proceedings Vol. XVII, p. 1184. See also P. DEBIJE Ann. d. Phys. (4) 46, p. 809, 1915

³⁾ Unless argon should be more-atomic in the liquid state, which is not made probable by the following.

improbable if not impossible great distance, which the centres of the atoms should have then (see table I).

The distance of the interfering particles calculated with (1) however agrees with the distance of the centres of neighbouring molecules, when we think us these arranged as the centres of spheres packed possibly close together. This distance is found in the last column of table I (M = molecular weight, d = density). Small deviations, as far as they do not fall within the limits of experimental accuracy, might be ascribed to deviations from the spherical form or to the circumstance that will be discussed in § 6.

From this we think it justified to draw the conclusion, that the intense diffraction ring found above is caused by the interference of Röntgen light diffracted by neighbouring *molecules*^{1) 2)}.

For benzene too the above mentioned agreement between a and the distance of neighbouring molecules arranged in closest packing has been stated. From this we think it evident that the above considerations also hold for this substance in contradiction with the opinion of DEBIJE and SCHERRER (l.c.) that this diffraction ring should be due to the atoms in the molecule.

§ 5. When our view that the observed diffraction ring is due to the interference of Röntgen light diffracted by neighbouring molecules is right, the dimensions of these diffracting particles may no longer be neglected compared with their mutual distance and we may ask:

1) This does not involve that we have to do with the cooperation of only two molecules at a time. On the contrary, as far as it is not due to the particular form of the relation between the quantity of Röntgen light and the blackening of the film caused by it, the relative sharpness of the diffraction ring might point at a cooperation of more molecules at a time.

These molecules might then be arranged in the liquid in groups more or less regularly under the influence of the forces which below the melting point condition the regular structure in the crystalline state.

In this way f.i. *both* rings of argon might be explained by assuming that in the liquid a great number of groups is present in which the atoms are arranged in a centered cubical lattice. The mentioned rings correspond then to the planes (110) and (211), the edge of the lattice would be 4,65 Å. For the distance of two neighbouring atom centres follows then again 4,0 Å as in table I.

Because of the perfect analogy in the behaviour of oxygen and argon we should have to replace for oxygen these atom centres by molecule centres. [Later experiments have shown that the ratio of the values of $\sin^{1/2} \varphi$ for the two rings does not quite agree with the ratio 1:√3, as should be the case if the supposition made above were valid. Added in the translation].

2) The possibility of this has already been acknowledged by DEBIJE and SCHERRER (l.c.).

in how far may we regard the distance calculated with (1) as the distance of the *centres* of the molecules?

As in reality the electrons are the diffracting particles, this question may only be answered when the true position of the electrons in the molecule is known for every instant.

In order however to form us still an opinion in this problem we shall consider the case of molecules each consisting of a nucleus (which is supposed not to contribute to the diffraction) and one electron that is freely moving in a sphere with radius r (so that it passes in all volume elements equally long times). A system of arbitrarily orientated pairs of such molecules all with the same distance a between the molecule centres gives then in a direction which makes an angle φ with the direction of the incident light an intensity proportional with

$$1 + 9 \frac{\{\sin \alpha r - \alpha r \cos \alpha r\}^2}{\alpha^6 r^6} \cdot \frac{\sin \alpha a}{\alpha a} \cdot \dots \dots \dots (2)$$

when

$$\alpha = \frac{4\pi}{\lambda} \sin \frac{\varphi}{2} \dots \dots \dots (3)$$

This expression may be easily deduced by an extension of the calculation given by EHRENFEST for the case of two simple diffraction centres.

When r is not small compared with a , the first maximum does no longer correspond with the relation (1). In this case an other factor must be substituted for 7,72 in this formula. When f.i. we take $a = 4 \text{ \AA}$, $r = 1,25 \text{ \AA}$, this factor is 7,42.

Evidently the influence of the dimensions of the molecule is small. The more will this be the case as the (mean) density of the electrons in the molecule is greater in the central parts than near the periphery.

When the molecules come so near to each other, that they are in contact the influence is greater. For the simple molecule models, described above, the factor in (1) would then become 10% smaller.

§ 6. *Water.* The blackening which is found in the diffraction image for water round the above mentioned diffraction ring seems to point at a rather great number of pairs of molecules with a mutual distance smaller than that which we shall call here the normal one¹⁾. On this supposition the limit of this blackening

¹⁾ With the above is in good agreement, that in table I the mean distance (3,6 Å) for water is smaller than the normal one (3,75 Å).

$\gamma = 46^\circ$) corresponds to the smallest distance between the centres of two neighbouring molecules. Formula (1) gives for this 2,4 Å.

The further examination of the blackening in the diffraction image of the liquids thus gives a direct method of research for the way in which the molecules are distributed in the liquid as to their mutual distances. Some conclusions may be drawn then also on the field of force of the molecules.

The fact, that in water a relatively great number of pairs of molecules occurs with a distance smaller than the normal one will be related with the peculiarities in the thermodynamic properties by which water is regarded as an associating substance. However, we do not find an extraordinarily great number of double or multiple molecules which should have been formed by juxtaposition of simple molecules so as to lie as close as possible to each other.

§ 7. *Oxygen and argon.* By analogous considerations as in § 6 we probably must ascribe the second weak ring for oxygen and argon to pairs of molecules which touch each other¹⁾.

According to (1) this would give for the distance of the centres for oxygen 2,4 Å, for argon 2,3 Å.

Because of the last remark of § 5 these values might however still undergo a small variation.

Comparing these results with those obtained for water we find: firstly, that in oxygen and argon there is a considerably smaller number of pairs of molecules with a distance below the normal one, secondly that for oxygen and argon in the greater part of these molecule-pairs the molecules are lying together as close as possible.

We might ascribe this different behaviour to a difference in the fields of force: the water should have then a more intense field, which extends over a greater distance, while oxygen and argon should have a field of force which makes itself more felt in the immediate neighbourhood of the molecule. In this way the dipolar character of the water molecule becomes manifest on one hand, the quadrupolar (resp. perhaps octopolar) character of the oxygen and the argon molecule (atom) on the other hand.

¹⁾ See also p. 122 note 1.

W. H. KEESOM and J. DE SMEDT: „On the diffraction of Röntgen-rays in liquids.”

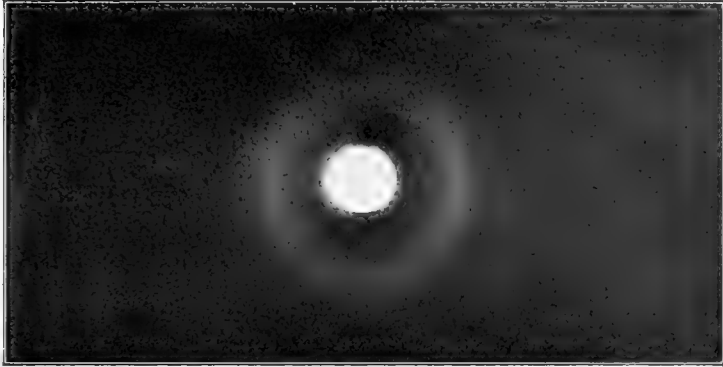


Fig. 2.
Oxygen, with $K\alpha$ -rays of copper.

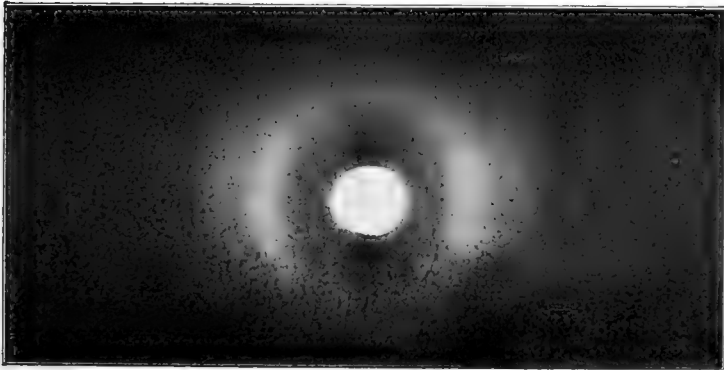


Fig. 3.
Water, with $K\alpha$ -rays of copper.



Physics. — “*The crystal structure of germanium*”. By Dr. N. H. KOLKMEIJER. (Communication N^o. 11 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of April 29, 1922).

§ 1. *Introduction.* From a medical-biological point of view too, a possibly complete knowledge of the quadrivalent elements as f. i. C and Si will be of great importance. The only one among the elements of the fourth group of the periodic system the crystal structure of which has not yet been investigated is germanium¹⁾.

For this reason the author undertook the investigation of this structure with the same apparatus that had already been used in the investigation of tin²⁾ and in that of NaClO₃ and NaBrO₃³⁾, that has been described in preceding papers. Only the diaphragm of lead in the camera was replaced by one of tin⁴⁾ while before it a Ni-filter of 0,01 mm. thickness was placed in order to weaken the β radiation from the Cu-anticathode. The germanium (from Dr. Th. SCHÜCHARDT, Görlitz), in the form of a fine powder, was cemented to a thin glass rod, with Canada-balsam.

§ 2. *The crystal structure.* The observations were in good agreement with a structure like that of diamond. In the table this is evident from the satisfactory agreement between the values of $\sin^2 \frac{1}{2}\theta$ ⁵⁾ derived from the observations with the calculated ones. For the latter we chose as value of the lattice parameter $a = 5,61 \text{ \AA}$. From the density at 20°, viz. 5,459⁶⁾, the atomic weight 72,418⁷⁾ and the number of AVOGADRO $6,062 \cdot 10^{23}$ we deduce $a = 5,594 \text{ \AA}$.

¹⁾ As has been remarked by D. COSTER (These Proceedings 21, 1294, 1919) the knowledge of this structure might also be of importance for the question of the eventual existence of binding rings of circulating electrons.

²⁾ A. J. BIJL and N. H. KOLKMEIJER. These Comm. Nos. 1 and 2. These Proceedings 21, 405, 494, 1918.

³⁾ N. H. KOLKMEIJER, J. M. BIJVOET and A. KARSSSEN. These Comm. N^o. 5, These Proceedings 23, 644, 1920.

⁴⁾ W. H. KEESOM and J. DE SMEDT. These Comm. Nr. 10. These Proceedings 25, 118, 1922. By a sufficiently high tension the L-radiation of the Pb might namely be excited by the heterogeneous radiation of the Cu, which would cause a blackening of the film. For tin this is much less probable.

⁵⁾ θ is the angle between the rays incident on the substance and those diffracted by it.

⁶⁾ CL. WINKLER, Journ. f. prakt. Chem. 34, 177, 1887.

⁷⁾ J. H. MÜLLER, Journ. Am. Chem. Soc. 43, 1085, 1921.

| Observed. | | | | Calculated ¹⁾ . | | | |
|------------|-------------------------------------|----------------|-------------------------------------|----------------------------|----------------|-------------------------------------|------------|
| | | | | α -lines. | | β -lines. | |
| Intensity | $\sin^2 \frac{1}{2}\phi \cdot 10^3$ | $h_1 h_2 h_3$ | $\sin^2 \frac{1}{2}\phi \cdot 10^3$ | Intensity | $h_1 h_2 h_3$ | $\sin^2 \frac{1}{2}\phi \cdot 10^3$ | Intensity |
| vs | 59 | 1 1 1 | 56 | 1.3 | | | |
| vf | 124 | | | | 2 2 0 | 122 | 1.5 |
| s-vs | 153 | 2 2 0 | 151 | 1.5 | | | |
| fff | 168 | | | | 3 1 1 | 167 | 1.1 |
| s-vs | 207 | 3 1 1 | 207 | 1.1 | | | |
| f | 249 ⁵ | | | | 4 0 0 | 243 | 0.4 |
| f | 296 | 4 0 0 | 301 | 0.4 | 3 3 1 | 289 | 0.6 |
| m-s | 363 | 3 3 1 | 358 | 0.6 | 4 2 2 | 363 | 1.0 |
| s-vs | 454 | 4 2 2 | 452 | 1.0 | | | |
| f (double) | 511 | 3 3 3 5 1 1 | 508 | 0.6 | 5 3 1 4 4 0 | 532 ⁵ 487 | 0.7 0.4 |
| f | 599 ⁵ | 4 4 0 | 603 | 0.4 | 6 2 0 | 609 | 0.6 |
| s-m | 652 | 5 3 1 | 659 | 0.7 | 5 3 3 | 654 | 0.3 |
| m | 745 | 6 2 0 | 753 | 0.6 | 5 5 1 7 1 1 | 776 | 0.5 |
| f | 801 | 5 3 3 | 810 | 0.3 | | | |
| ff | 848 | | | | 6 4 2 | 852 | 0.9 |
| f | 892 | 4 4 4 | 904 | 0.2 | 5 5 3 7 3 1 | 898 | 0.6 |
| s m | 948 | 5 5 1 7 1 1 | 960 | 0.5 | | | |
| f | 966 | | | | 8 0 0 | 974 | 0.1 |
| m | 994 | | | | 7 3 3 | 1019 | 0.2 |

From the fact that of C, Si, Ge and Sn we know modifications with the same structure as diamond, while this is not the case for Ti, Zr and Th, we might conclude that C and Si are somewhat more intimately connected with the elements of group IVb than with those of group IVa.

To Prof. Dr. W. H. KEESOM I am much indebted for his interest and his kind help in this investigation.

¹⁾ In the calculation of the intensities, only the structure factor, the LORENTZ-factor and the number of planes factor have been used, not the polarisation factor and the temperature factor.

Physiology. — *“An Objective Method for determining the Coagulation-time of Blood.”* By R. J. WOLVIUS. (Communicated by Prof. A. A. HIJMANS VAN DEN BERGH.)

(Communicated at the meeting of December 23, 1921).

The usual methods for determining the coagulation-time of blood aim at detecting the right moment at which the phase of complete solidification of the blood has just set in.

At first I myself adopted the method suggested by FONIO and FRANK, viz. by observing, with strict precaution, the coagulation of the blood on a watchglass and by noting down the moment at which the phase of complete solidification had apparently been reached. However I was always in doubt whether complete solidification had been accomplished at a certain moment, or whether it had not, so that I always hesitated in fixing the right moment.

In this connection HAYEM¹⁾ says: “On sait, en effet, que la solidification du sang ne se fait pas brusquement, c’est à dire d’un seul coup, à un moment précis. Le phénomène, évolue d’une manière progressive, à tel point, que pendant une période relativement assez longue, on reste dans l’hésitation, en se demandant si la prise en gelée est effectuée ou n’est encore qu’imminente.”

What tells most against these methods, is that the degree of solidification has to be determined by subjective observation. I, therefore, looked for some phenomenon that goes on *pari passu* with the solidification and admits directly of measurement. I found that phenomenon in the turbidity which attends the salting out of fibrin and consequently decided to measure it. Preliminary experiments had shown that at the very outset of thickening of the blood a clouding commences that increases with the further progress of the thickening and ultimately remains stable as soon as coagulation has reached its completion. Now, it being my purpose to observe the time in relation to solidification, I might as well ascertain the time taken up by the clouding process. In order to measure this growing turbidity I made use of a new apparatus, the extinction

¹⁾ HAYEM, *Du Sang*, quoted from MARCEL BLOCH, *La coagulabilité sanguine* pag. 22. Thèse, Paris 1914.

meter¹⁾ of Dr. W. J. H. MOLL, which enables us to measure the turbidity from moment to moment.

The principle of this apparatus may be discussed in a few words:

A powerful light-source is firmly set up between two surface thermobatteries I and II, after MOLL. They are both connected to a mirror-galvanometer, thus counteracting each other. Between the lamp and the thermobattery I is placed a cuvette filled with water; between the lamp and the thermo-battery II a cuvette filled with the blood-plasm.

Consequently the light that is directed on to the thermo-batteries is weakened on the one side by water, and on the other by blood-plasm. Through displacement of one of the thermo-batteries or through changing the position of the lamp the unevenly weakened light may be made to fall upon the thermo-batteries with equal force. The two thermo-electric currents thus elicited, will then be equal, the galvanometer will receive a current 0, the image reflected by the mirror will occupy the 0-position. The apparatus has then been "adjusted". The slightest change in the turbidity of the plasm disturbs the equilibrium and yields a deflection of the galvanometer; the apparatus acts so quickly that after a contingent sudden change in the turbidity the reflected image will come to rest again within a few seconds. Moreover a procentic measurement may be taken of the changed turbidity with the aid of a so-called compensation-switch.

Now our procedure is as follows: Into a sterile, dry Record-syringe of 10 c.c. with a sharp, dry needle, 1 c.c. of a clear sterile solution of 1% potassium oxalate in 0.85% common salt is sucked up; the needle is inserted into a cubital vein and the blood is aspirated to 10 c.c. Due regard should be given to an easy flow of the blood into the syringe, so that no air is drawn in along with it. The mixture thus obtained, is centrifugalized during 20 minutes in sterile centrifugation-tubes, which causes the blood-corpuscles and the blood-platelets to precipitate and the supernatant, more or less turbid plasm can be pipetted off and transmitted to sterile tubes. Three c.c. of this oxalate-plasm (measured very carefully with sterile pipettes) are put into pure, and dry cuvettes. The cuvettes used by me are made of the same glass and have precisely the same dimensions, so that not only the thickness of the fluid-layer, but also the level to which the cuvette is filled, is always the same in every one of them; in other words the contact-plane

¹⁾ Dr. W. J. H. MOLL, Een extinctiemeter. Verslag Koninklijke Akademie van Wetenschappen, Wis- en Natuurkundige Afdeling, 27 Maart 1920. Deel XXVIII.

between plasma and glass is the same. This cuvette is placed in another one of special construction, which acts as a thermostat, is filled with water and is heated electrically.

The measurement proceeds as follows:

The cuvette is placed in the thermostat so as to make the light of the lamp reach the thermo-battery II and pass through the plasm. By its side, in the same thermostat, stands a test-tube containing $1\frac{1}{2}$ c.c. $\frac{1}{2}\%$ CaCl_2 . The extinctionmeter is "adjusted". Then follows a 20 minutes' wait, after which the plasm and the CaCl_2 will be of the temperature of the thermostat and the galvanometer will be completely quiescent and in the zero-position. The work-room is made semi-dark and from this moment photographic readings are taken from the galvanometer. A registering instrument is used that is moved by a perfectly reliable clockwork.

After some moments the $1\frac{1}{2}$ c.c. $\frac{1}{2}\%$ CaCl_2 are added to the plasm, the whole mixture is rapidly stirred for half a minute with a sterile glass rod and is then left to itself. The galvanometer then traces on the sensitive paper of the registering instrument the "turbidity-curve".

Fig. 1 is a faithful reproduction (natural size) of such a curve, in

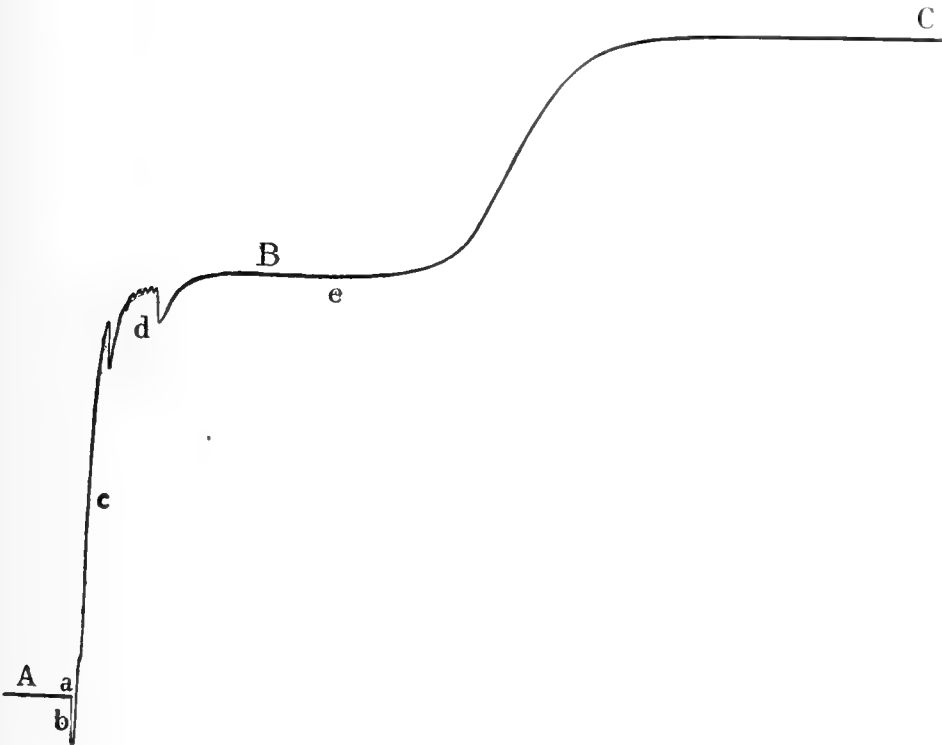


Fig 1.

which three horizontal portions *A*, *B*, and *C* are to be distinguished.

A indicates the motionless phase of the galvanometer during the time when there is only the oxalate-plasm between light-source and thermo-battery; *a.* indicates the moment when CaCl_2 is added; the first moment the plasm becomes clearer, see *b.*, which is owing to the dilution of the plasm. But directly after this the liquid becomes very turbid which is due to the forming calciumoxalate; the curve ascends almost vertically, see *c.*, and would gradually have reached the *B*-level, if not an irregular weakening of the light had been brought about by the stirring rod; the jerks in the curve at *d.* illustrate this irregularity, so that they have nothing to do with the process of turbidity. The calcium oxalate is not precipitated but remains in suspension; for a few minutes the galvanometer remains constant, as shown in the *B*-portion.

Up to this moment coagulation is out of the question. Solidification commences at *e.* at a certain moment, apparently quite independently from the initial turbidity (formation of calcium-oxalate), and simultaneously the second phase of turbidity begins. It is this portion of the curve that interests us most. Its shape is an objective illustration of the coagulation process.

It appears that this coagulation starts very slowly, then proceeds more quickly until a maximum rate is attained, after which a retardation sets in again until the terminal value is ultimately reached.

I will not discuss here the nature of this curve, but only point to the method, which enabled me to typify any given portion of the curve by a figure. I note the exact time at which certain levels, e.g. $\frac{1}{4}$ and $\frac{3}{4}$ of the difference of the *B*-, and *C*-level are reached; the time-difference is my control-number.

My researches were performed in the Physical Laboratory of the Utrecht State-University, where I had the freedom of the instruments.

Utrecht, December 1921.

Physiology. — “*A contribution to the physiology of the electrical organ of Torpedo*” By Prof. F. J. J. BUYTENDIJK. (Communicated by Prof. G. VAN RIJNBERK).

(Communicated at the meeting of April 29, 1922).

In the winter of 1911 I had the opportunity to investigate the function of the electrical organ of *Torpedo* in the Zoological Station of Naples. The aim of part of this research was to study the magnitude and character of its discharges under different circumstances. For this purpose a string-galvanometer (large type of EDELMANN) was available at Naples and with this apparatus I made many records. From these records and from test-records of the apparatus it appeared, that the string-galvanometer is not the most suitable instrument for the registration of the discharges of the organ of *Torpedo* which reach their maximum within 0,002—0,003 sec. This does not astonish us in connection with the investigations of GARTEN¹⁾. For this reason I intended to continue this research with an apparatus more suitable for this purpose (oscillographion, FUJI²⁾, string-electrometer, CREMER³⁾). However, as circumstances prevented me from carrying out this plan, I now communicate the results of my research.

MAREY, SCHÖNLEIN and GOTCH⁴⁾ have already observed that the reflex-discharge of the electric ray has a rhythmical character. In many records I found that as a rule many discharges succeed each other,

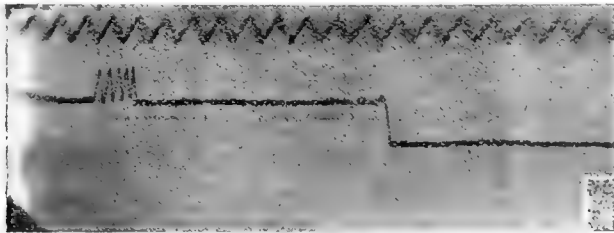


Fig. 1. Reflex-discharge in *Torpedo* after mechanical stimulation.
Test-record 4 volt. Time $\frac{1}{60}$ sec.

1) GARTEN. Abh. d. Kgl. Sächs. Ges. d. Wiss. 1899.

2) FUJI. Journ. of the College of Science Univers. Tokio 1914, Vol. 37.

3) CREMER. Sitz. Ber. Physiol. Gesellsch. Berlin 1912. Mediz. Klinik 1912, N^o. 42.

4) S. GARTEN. Handb. d. Vergl. Physiol. 3e Bd. 2e H., p. 177.

mostly 5—8 in number with an interval of 5σ . Fig. 1 represents one such discharge, where the shocks came with an interval of $5,6\sigma$. CREMER found an average of $5,6\sigma$ in reflex-discharge. Most striking in these rhythmical discharges is the regularity and the equal amplitude of the single shocks, as appears clearly from my figure. In the periodical discharges after stimulation of the nerve of the excised organ, I never obtained such regularity and as a rule unequal amplitude. Usually the shocks diminish gradually, sometimes they first increase, then decrease. Fig. 5*a* and 5*b* illustrate this more clearly. The periodical discharges in reflex-action therefore give the impression of being caused by a series of central impulses from my nervous system, whereas the periodical discharges after stimulation of the organ or the nerve seem to be due to secondary self-stimulation. This is especially and to a greater extent true in the case of the stimulation of the nerve. After direct stimulation of the organ usually only two small, secondary discharges occur, provided that the nerve has been cut at the very spot of its entrance into the organ. FUJI however has registered reflex-discharges (in *Astrape japonica*) in which only two shocks occurred in every group followed by a small one. The same result was also obtained after stimulation of the nerve stem. For this reason FUJI believes that the successive discharges occur by self-stimulation. The solution of this question has importance for the question which has been solved by GARTEN¹⁾ in *Malapterurus*, i. e. in how far the discharges of both organs occur simultaneously.

In a detailed research BERNSTEIN and TSCHERMAK²⁾ have tried to find out whether the current which the electrical organ produces during activity is caused by a concentration-chain or whether a so-called chemical chain here causes the difference in potential. To solve this question the temperature-coefficient of the force of the current in the organ was investigated within certain limits of temperature.

From theoretical considerations it is known, that in a concentration-chain the E. M. F. is nearly proportional to the absolute temperature. BERNSTEIN already had found a positive temperature-coefficient for the current in muscles and nerves and within normal limits of temperature the E. M. F. proved to be nearly proportional to the absolute temperature.

In their study on the electrical organ the authors mentioned above

¹⁾ GARTEN. Zeitschr. f. Biol. 1910. Bd. 54. S. 399—430.

²⁾ BERNSTEIN und TSCHERMAK. Pflügers Archiv. 1906, p. 112.

always stimulated the nerves of the organ by means of a single induction-shock (make-induction) and read the deviation of a galvanometer with not too great inertia on a scale. The deviations of such galvanometers are nearly proportional to the average E. M. F. of short currents, if the external resistance and the path of the current remain constant. The latter condition, however, was surely not complied with at different temperatures.

From the investigations of GORTZ on the capillary electrometer it had already become known that the velocity of the movement at low temperature (3° C.) is retarded and differs rather strongly from that at moderate temperature ($15-20^{\circ}$ C.). Such change in the record of the current must magnify the movements at low temperature. In that way - the difference with those found at higher temperature is bound to become smaller than corresponds to reality and the observed temperature-coefficients must be too small as GARTEN has already observed. Moreover, it has become evident from the experiments of SCHÖNBEIN and GARTEN, that after indirect stimulation of the electrical organ by induction-shocks a repeated discharge frequently occurs, which of course does not show up with the slow galvanometer.

My own experience has shown that especially in the cooled organ this repeated discharge occurs very frequently. In this way the very low temperature-coefficients, found by BERENSTEIN and TSCHERMAK may partly be explained.

At any rate, it seemed advisable to try to secure more data on the process and the E.M.F. of the shock. Of freshly caught specimens of *Torpedo marmorata* and *T. ocellata* the electrical organ was prepared free with its nerves after removal of the skin. The organ was now enclosed between two zinc electrodes by means of two rubber rings. Two bars for the conduction of the electrical shock were attached to the zinc electrodes.

The conductors were passed through a rubber stopper which also held the platinum electrodes used for the stimulation. This rubber stopper served to close a glass-vessel, in which the organ could be enclosed and through which a stream of liquid could be passed. The strength of the electrical discharge could thus be studied under different circumstances.

Moreover, a thermometer was inserted into the stopper. If one allows the liquid to flow into the vessel through the lower tube (Fig. 2) and to leave the apparatus by the upper one, it is possible to regulate conditions so as to keep the organ in the fluid and to keep the nerves in the air.

This arrangement had the advantage that it enabled me to repeat the indirect stimulation under very constant conditions. In this way one succeeds in keeping the organ in good condition for 2—3 hours,

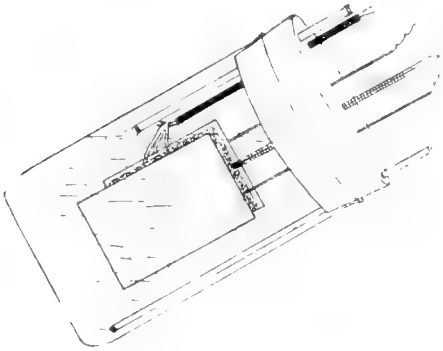


Fig. 2. Apparatus for study of electrical discharge in different fluids, gases and temperature.

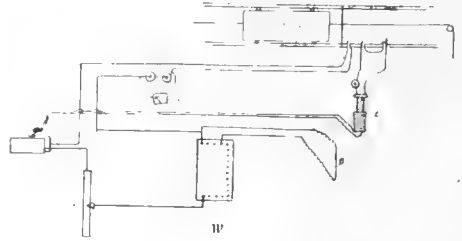


Fig. 3.

lo = electr. organ *s* = string-galv.m.
l = slate-resistance *i* = induction-app.
v = volt-meter *phz* = apparatus for
w = resistance-box photo-gr. registrat.

so that if one stimulates once every 15 minutes the deviations of the galvanometer remain constant.

The discharge was led to an ordinary resistance-box and a slate-resistance (of 800,000 Ω). From the resistance-box a circuit could be branched off to the string-galvanometer. By means of a key, connected with the recording apparatus, a definite potential difference could be thrown into the chief circuit for the purpose of testing the movements of the string (Fig. 3).

A tuning fork of 50 vibrations per second marked the time on the photographic plate, while a very sensitive signal of DEPRÉZ indicated the moment of stimulation. The nerves were stimulated by means of induction-shocks. Sometimes part of it was thrown into the string-circuit so as to have the string itself mark the moment of stimulation.

It is clear that this method does not enable one to study the question of the relation of a stimulus to its effect.

This question has been thoroughly investigated by FUJI with the oscillographion.

In my experiments I could not state anything but the fact that a weaker stimulus gave a less noticeable effect than a strong one and

that make induction-shocks are more effective than break-shocks (Fig. 4).

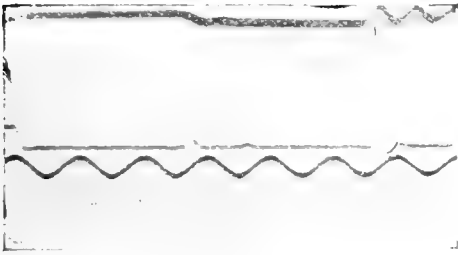


Fig. 4. Example of discharge after indirect nerve stimulation with make and break induction shock.

To get an impression of the conditions on which the magnitude of the discharge depends, I first investigated the question whether organs which had been kept in different liquids for some hours, as a result showed a change of the discharge-shock. Of course, the nerves were always stimulated with maximal stimuli.

In this way it appeared that an organ (without skin) kept in:

Experiment 1.

2,5% NaCl-solution lost its irritability after three hours. The same thing was true for sea water. In Fühner's solution + urea¹⁾ the irritability strongly diminished after three hours.

Experiment 2.

Organ 1: in (NaCl 2,5% + KCl 0,1%) no shock could be obtained after 40 min.

Organ 2: in (NaCl 2,5% + CaCl₂ 0,2%). After 40 min. the shock had diminished slightly.

Organ 3: in F. sol. after 40 min. shock not changed.

Experiment 3 (see fig. 5).

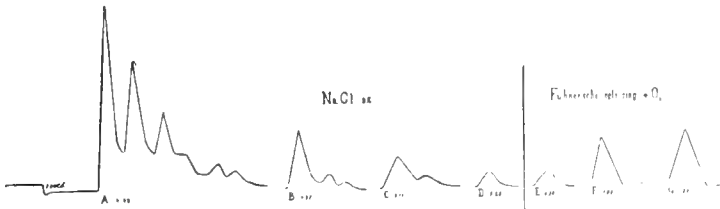


Fig. 5.

A preparation made from *Torpedo marmorata* (size 15 c.m.) from 3.50—4.10, Organ 1 is put into NaCl 3%. From 3.50—5.28 four records were made (fig. 3. a, b, c, d), the preparation was then put into Fühner's solution + O₂. After about 60 min. record e, after another 38 min. record f, after 20 min. record g.

¹⁾ Fühner Zeitschr. f. allgem. Physiol. (1908) Bd. 85. 485.

Used solution was:

| | | |
|---------------------------------|-----|-------------------|
| Na ₂ CO ₃ | 0.2 | } per 1 L. water. |
| CaCl ₂ | 0.2 | |
| KCl | 0.1 | |
| NaCl | 20. | |
| Urea | 25. | |

It appears that after the discharge has decreased in the NaCl solution, it again increases in Fühner's solution + O₂.

The other organ (2) has been kept in moist air from 4.10 until 6.47, then it is put into Fühner's solution + O₂. It becomes apparent that this organ also shows a considerable increase in magnitude of the discharge after 30 minutes.

The result of experiment 3 is therefore that O₂ causes the shock to increase and that sol. F. shows the same activity even though the discharge had been weakened by an immersion in NaCl-solution.

Experiment 4 (Fig. 6 and Fig. 7).

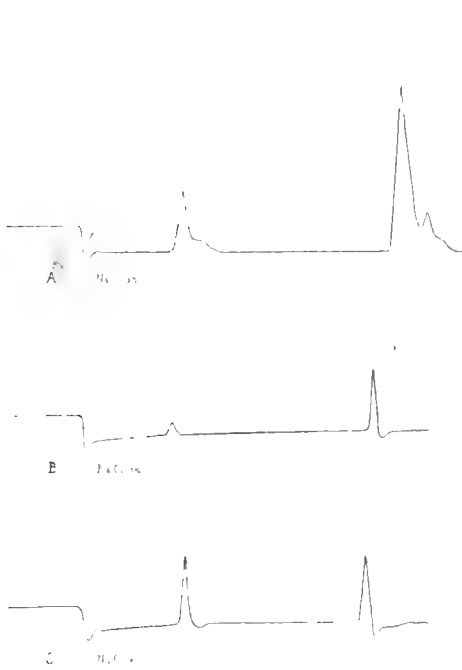


Fig 6.

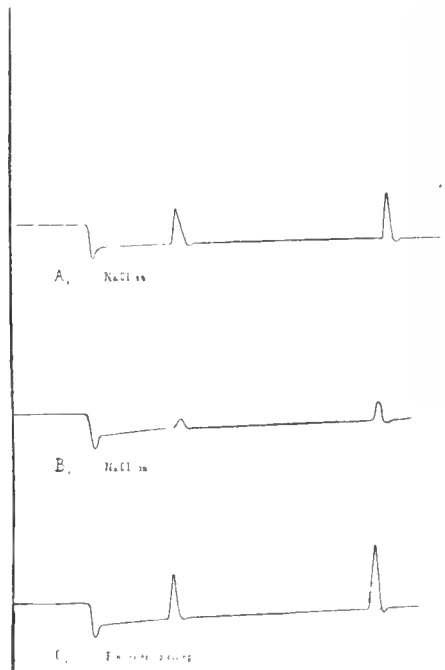


Fig. 7.

Preparation of small Torpedo (15 c.m.).

Organ 1 (Fig. 6): At 3.53 in 3% NaCl. Record A. After two hours record B. O₂ is now bubbled through the NaCl. After 30 min. record C.

Organ 2 (Fig. 7): At 4.50 in 3% NaCl. Record A₁. After 70 min. record B₁. NaCl replaced by Fühner's solution. After 30 min. record C₁.

Result: O₂ restores the discharge even if the organ remains in NaCl-solution. Sol. F. restores the discharge which has been diminished in NaCl. solution.

Experiment 5.

The preparations were made at 10.30 in the morning.

Organ 1: kept for 4 hours 40 min. in F. sol. poor in oxygen (boiled).

Record a: deviation is 0.25 volt. After 14 min. exposure to the air.

Record b: deviation is 0.31 volt. After the preparation had been kept for 23 min. in well-aerated F. sol.

Record c: deviation is 1.4 volt.

Organ 2: kept for 4 hours 30 min. in F. sol. (O₂ bubbling through).

Record *a*: deviation is 3 volt (followed by a series on spontaneous discharges).

In F. sol. free of O₂ the deviation diminishes considerably. After the preparation has been kept for a long time in F. sol. rich in O₂, a repeated discharge follows after one indirect stimulation.

In two other experiments in duplicate it could be shown that also after keeping the organ in F. sol. which had been saturated with H₂ and more so yet in one with CO₂, O₂ causes the deviation to increase.

After this series of experiments another one followed in which the same apparatus was used (Fig. 2). The Fühner's solution, poor in O₂ or saturated with, it was here kept at certain definite temperatures by immersing the whole apparatus in a thermostat.

Experiment 8.

Organ 1: Temp. 18°. Deviation about 25 volt. Latent period 5,5 τ .

After 30 min. Temp 11°. Deviation 24,2 volt. Latent period 6,8 τ .

After 22 min. Temp. 28°. Deviation 0,3 volt. Latent period 4,2 τ .

Organ 2: Temp. 18°. Deviation 20,6 volt. Latent period 6,4 τ .

After 40 minutes: Temp. 30°. Deviation 0,25 volt. Latent period 3,4 τ .

After 26 minutes: Temp. 15°. Deviation > 4 volt. Latent period 6,5 τ .

Experiment 9.

Piece of organ of large Torpedo between zinc electrodes, two nerves being intact. Thermometer lies in immediate neighbourhood of organ. Length of nerves 15 m.m. Distance of stimulating electrodes 3 m.m.

| Temp. degrees C. | Time. Hour. | No. | Test. | Test deviation m.m. | Discharge Volt. | Lat. per. in τ . |
|------------------|-------------|----------|-----------|---------------------|-----------------|-----------------------|
| 20 | 5.05 | <i>a</i> | 4 volt | 5 | > 40 | 5.2 |
| 13 | 5.15 | <i>b</i> | 4 volt | 5 | \pm 30 | 7.5 |
| 7.5 | 5.37 | <i>c</i> | 4 volt | 5 | 32 | 12 |
| 6 | 5.53 | <i>d</i> | 4 volt | 5 | 10.5 | 20 |
| 5 | 6.32 | <i>e</i> | 1/2 volt | 5.5 | 0.27 | 22.3 |
| 10 | 6.47 | <i>f</i> | 1/16 volt | 9 | 0.31 | 16 |
| 15 | 7.16 | <i>g</i> | 1/2 volt | 5.5 | 0.67 | 8.7 |
| 15 | 9 | <i>h</i> | 1/4 volt | 14 | 0 | |

As mentioned before we can not attribute any absolute value to the volt-values given for the discharges, since the galvanometer-records require a correction which can not be calculated very easily. After cooling, however, the string will more easily follow the potential difference, because it develops more slowly in the cold.

Whatever may be their absolute value we can see easily from

figures of exp. 9 that as long the organ is cooled, up to about $7,5^{\circ}$, the discharge diminishes slightly, though not very considerably. From $5-15^{\circ}$ a rapid decrease follows with a slight recovery. Then the organ apparently is dying.

The changes in deviation of the test-potential were obtained by changing the side-chain or the resistance, not by changing the sensitiveness of the string (tension).

Experiment 10.

Large organ, kept in F. sol. containing O_2 .

| Time. | Temp. | Test. volt | Deviation Test. m.m. | Discharge Volt | Latent Period in σ |
|-------|-------|---------------|----------------------------|-------------------|---------------------------------|
| 4.23 | 5 | 1 | 11.5 | 0.33 | 12.26 . |
| 4.38 | 10 | 1 | 14 | 0.49 | 9.33 |
| 5.53 | 19 | 1 | 7.5 | 3.3 | 5.6 |
| 5.14 | 26 | 1 | 7.5 | 0.67 | 4.66 |

The temperatures given are presumably not those of the inside of the organ because the temperature changed too rapidly. Consequently the large organ could not have assumed the temperature of the environment.

Heating to above 22° gives a considerable decrease as appears from:

Experiment 11.

At 3.05 'o clock. Temp. 21° . 1 volt = 2,6 m.m. Deviation 25 m.m.

At 3.30 'o clock. Temp. 28° . 1 volt = 2,6 m.m. Deviation 2,1 m.m.

The rise in temperature has diminished the deviation to $1/10$.

Experiment 14.

At 5 'o clock. Temp. 20° . 1 volt = 5,5 m.m. Deviation 32 m.m.

At 5.30 'o clock. Temp. 25° . 1 volt = 5 m.m. Deviation 17 m.m.

The rise in temperature has caused the deviation to diminish to $1/2$.

In Fig. 8 and 9 the string-record of the discharge at different temperatures has been pictured together with the test-record. I have reconstructed it to the best of my ability from the not absolutely focussed photographs.

Large organ in F. opl. at 28° C. (since 12.55).

| Time. | Test. 1 volt | Deviation. |
|-------|-----------------|------------|
| 1 11 | 5 m.m. | 35.5 m.m. |
| 1 27 | 5 m.m. | 34 m.m. |

Now 8 stimuli are given at intervals of 30 sec.

1.31 | 5 m.m. | 4.8 m.m.

In that way it is evident that at high temperatures fatigue occurs very rapidly. A attempt to study the influence of O_2 at different temperatures could not be carried out systematically.

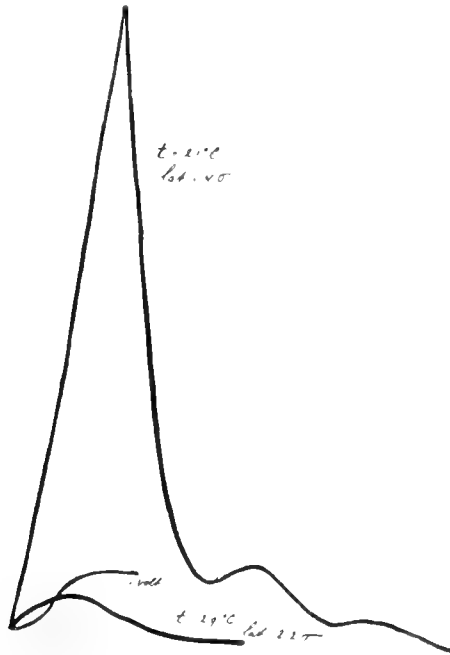


Fig. 8.

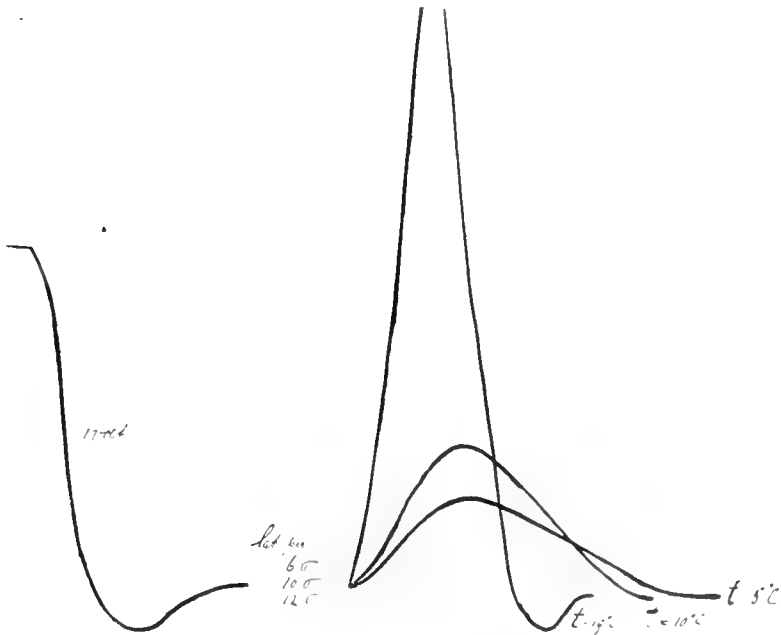


Fig. 9.

From the experiments it appeared however that at high temperatures (22° – 28°) O_2 did not cause an increase in discharge. The latter was the case at lower temperatures. Experiments on the influence of narcotics had to be given up at an inopportune moment.

Fig. 10 demonstrates that by chloral-hydrate the discharge disappears nearly completely.

In the apparatus nerve and organ were kept at the same temperature. It seemed important in order to judge about the change



Fig. 10a.

a. Record of discharge small electrical organ). Test $\frac{1}{4}$ volt.

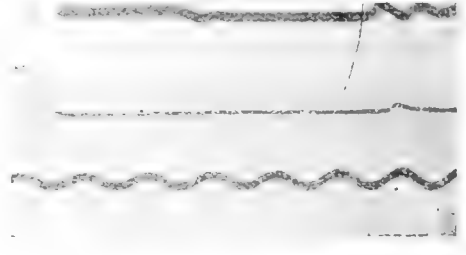


Fig. 10b.

b. The same after exposure to chloral-hydrate dissolved in Fühner's solution.

in the values for the latent period, to submit the nerves separately to changes in temperature.

Experiment 16.

Preparation of large Torpedo (28 c.m.) made between 11.45 and 12.45 and put into apparatus.

Piece of organ with two nerves, the nerves led through glass tubes, in which stimulating electrodes. Tubes surrounded by glass-mantle, in which water circulates at different temperatures.

After the experiment has been ended a control is made by tying off the nerves, which causes a complete breaking of the conduction.

The magnitude of the deviation remained the same although the temperature of the nerve varied from 20° – 6° .

The values of the latent periods actually were lower at lower temperatures. The measurements are, however, not sufficiently accurate to allow a calculation of the velocity of the conduction. That, however, the differences in latent period found in the other experiments are due to changes in the electrical organ, is evident from the fact, that in this experiment the difference between 6° – 20° only amounted to 1.8σ .

Having thus obtained an impression on the influence of temperature O_2 and different salt-solutions on the strength of the discharge as a response to indirect stimulation. I have tried to study the gaseous exchange of the electrical organ in rest and during activity.

For this purpose the electrical organ was enclosed in a very thin

dialysing sac of collodion. The oxygen of the surrounding liquid passes through these sacs without difficulty, as could be shown in preliminary experiments, but only a very small quantity of organic substances passed through so that the method of WINKLER for the determination of O_2 dissolved in water, could be used with a slight correction. This very useful method of WINKLER can only be used in the absence of organic substances in the liquid or after a correction has been made¹⁾.

This dialysing sac was put into a bottle, which was completely filled with FÜHNER'S solution of known O_2 content. After some time (1—2 hours) a certain quantity of the contents of the bottle was again secured for a WINKLER'S determination of its O_2 percentage.

In order to stimulate the organ during its stay in the liquid, two silver electrodes were tied to the organ. Organ and electrodes were then put into the dialysing sac and immersed into the liquid. The organ was stimulated directly once every 5 sec.

The results are given in the following table:

TABLE I.

| Exp. No. | Weight organ in gms | Stim. + Not-stim. — | Time of resp. in hours. | Temp. ° C. | O ₂ consumed in cc. ¹ / ₁₀₀ N thio per hour and K.G. | |
|----------|---------------------|------------------------|-------------------------|------------|---|---------|
| | | | | | Not stimul. | Stimul. |
| 6 | 35 | — | 2 | 18 | 60 | |
| 7 | 36 | — | 1 1/4 | 18 | 62 | |
| 7a | 36 | + | 1/2 | 18 | | 103 |
| 8 | 41 | — | 1 | 21 | 220 | |
| 8a | 41 | + | 1 | 19 | | 220 |
| 9 | 57 | — | 1 | 21 | 103 | |
| 9a | 57 | — | 1 | 19 | 74 | |
| 10 | 18.3 | — | 1 | 21 | 306 | |
| 10a | 18.3 | + | 1 | 21 | | 440 |
| 12 | 28 | — | 1 | 6 | 136 | |
| 12a | 28 | + | 1 | 6 | | 160 |
| 13 | 41 | — | 1 | 19 | 93 | |
| 13a | 41 | + | 1 | 19 | | 100 |

¹⁾ See HENZE Abderh. Handb. der Biochem. Arbeitsmeth. III, p. 1067.

In the first place it became evident that though the results varied considerably — this is easily explained by the changing condition of weight etc. of the organ and the varying conditions for the diffusion of oxygen — the figures in the first place give a very definite idea about the gaseous exchange in the electrical organ. The electrical organ appears to consume 6—18 m.m³. O₂ per gram-hour, a quantity which is of the order of the O₂ consumption of the peripheral nervous system (THUNBERG)¹⁾ which consumes about $\frac{1}{10}$ of the quantity that is used by the central nervous system.

In 1883 WEYL tried to demonstrate some chemical changes in the electrical organ after it had shown vigorous activity. He found a change in reaction (hydrogen-ion concentration) i.e. an increase in acidity after activity. Moreover, he tried to estimate the production of CO₂ by the organ. WEYL found that 17,5 gms. produced 4 mgms. CO₂ in two hours. After stimulation he found a decrease instead of an increase. The alcohol-extracts of a stimulated organ and one which had not been stimulated, did not show any differences. The watery extract of the stimulated organ was larger. I myself have tried in vain to demonstrate the change in reaction after stimulation. I have tried to demonstrate two chemical substances in the electrical organ i.e. xanthin-bases and glycogen. This seemed to me to be of importance, because we know that the electrical organ must be derived from muscles in which both substances occur abundantly.

The xanthin-bases were determined according to the method of BURIAN:

100 gr. of the organ are boiled for 12 hours in 1 L. of 0,5 % H₂SO₄. After filtration the sulfuric acid is precipitated with Ba(OH)₂ and the liquid which is now alkaline is filtered. The filtrate is saturated with CO₂. The BaCO₃ is removed by filtering and the filtrate, after acidification with acetic acid, is evaporated down to 100 c.c. These 100 c.c. are boiled for some time with a smaller quantity of concentrated NaOH + Na₂CO₃ and filtered. The filtrate is acidified with HCl. A precipitate of xanthin bases now comes out on addition of an excess of NH₃ + AgNO₃. In this precipitate nitrogen can be determined according to KJEHLDAHL.

The following table gives the results of this investigation: (See Table 2, following page).

We may therefore conclude that the electrical organ contains no xanthin-bases or a negligible quantity.

Determinations of glycogen were made in two very large animals and in two young ones.

¹⁾ THUNBERG. Zbl. Physiol. 28 (1904). See also BUYTENDIJK. Kon. Ak. v. Wetensch. 1910 (615—621).

TABLE 2.

| | | Result. |
|----------|---------------------------|---------------------|
| Exp. 1. | 107,5 gm. electric organ. | Very slight precip. |
| Exp. 1a. | 55 gm. muscle | Heavy precip. |
| Exp. 2. | 106 gm. electric organ. | No precip. |
| Exp. 3a. | 120 gm. electric organ. | Very slight precip. |
| Exp. 4. | 122 gm. electric organ. | No precip. |
| Exp. 4a. | 52 gm. muscle | Heavy precip. |

The determination was made according to PFLÜGER:

TABLE 3.

| Exp. | Size of animal in c.m. | Quantity of organ. | % Glycogen. |
|------|---------------------------|--------------------|-------------|
| 1 | 60 } taken out of the | 313 | 0.051 |
| 2 | 45 } aquarium. | 128.8 | 0.031 |
| 3 | 15 freshly caught animal. | 20 | 0.787 |
| 4 | 5 6 specim.; just born. | 13.5 | 1.02 |

If we compare these results with those of BAGLIONI ¹⁾, we see that the glycogen values in exp. 1 and 2 are lower than those given by BAGLIONI (0,09 %), but of the same order. The figures in very young animals (exp. 3 and 4) are very much higher.

If the electrical organ functions by splitting up ion-proteids, we may expect salts to become free. This might be the explanation of the increase of the watery extract found by WEYL. The electrical organ reacts to mechanical stimulation, e.g. mincing or pressure, by strong activity. Therefore I have tried to divide electrical organs finely by gradually cooling and finally freezing them. In that way no discharges occurred. In centrifuging the frozen organ after it had been ground up, I could obtain a very complete separation of the organ-fluid. This fluid as obtained from stimulated and fresh organs, was used for the present research.

In the liquid thus obtained I made a determination of the ash-compounds, which led to the following results:

¹⁾ BAGLIONI. Hofmeister's Beiträge 1906. Bd. VIII, p. 456—471.

TABLE 4.

Ash (mgs per c. c. organ-fluid) determined after the wet method (SO₄ ash).

| Exp. | Not stimul. | Stimul. | Difference. |
|------|-------------|---------|-------------|
| 1 | 31.8 | 31 | - 0.8 |
| 2 | 30.4 | 31.2 | + 0.8 |
| 3 | 38.6 | 35.5 | - 3.1 |
| 4 | 26 | 28 | + 2 |

We see at once that there is no difference in ash-content in the fluid of a stimulated organ and of one which had not been stimulated. Moreover I made freezing-point determinations in both liquids.

TABLE 5.

 Δ in ° in organ-fluid.

| Exp. | Not stimul. | Stimul. | Difference. |
|------|------------------------|----------------------------|-------------|
| 1 | 2.12 | 2.215 | + 0.095 |
| | 2.12 | 2.21 | + 0.09 |
| 2 | 2.145 | 2.30 | + 0.155 |
| | 2.135 | 2.295 | + 0.160 |
| 3 | 2.16 | 2.23 | + 0.07 |
| | 2.15 | 2.24 | + 0.10 |
| 4 | 2.095 | 2.18 | + 0.085 |
| 5 | Ground when frozen. | Ground when warm (20°). | |
| | 2.08 | 2.25 | 0.17 |

From these experiments it appears that during activity substances pass into the organ-fluid which must be considered to be organic substance, because the ash-content is not increased, whereas the freezing point shows a very definite lowering.

However incomplete these investigations may be, I have felt the desirability of communicating them very briefly, the more because I shall most probably not be in a position to take up the whole problem once more and because the data published in the present paper, to my opinion, may be a stimulus to a continued research of the physical and chemical processes which take place during the discharge of the electrical organ.

Physiology. — “*On the Significance of Calcium- and Potassium-ions for the artificial Oedema and for the lumen of the bloodvessels*”. By RUDOLF J. HAMBURGER. (Communicated by Prof. H. J. HAMBURGER).

(Communicated at the meeting of March 25, 1922).

Of late years a series of researches have been carried out in the Groningen Physiological Laboratory, which demonstrated, among other things, that the solution used by SIDNEY RINGER in his remarkable experiments on the frog's heart, is not suitable for other organs of the frog. As known, this solution is composed as follows: NaCl 0,7 ‰, NaHCO₃ 0,02 ‰, CaCl₂·6 aq. 0,04 ‰, and KCl 0,01 ‰. HAMBURGER and BRINKMAN¹⁾ found that when, after the addition of a little glucose, this solution is allowed to perfuse the kidney, the glomerular epithelium does not retain any glucose. Systematical investigation, however, enabled them to modify the circulating fluid in such a way that the glomerular epithelium obtained the property to retain the physiological amount of glucose (0,060—07 ‰). This circulating fluid was of the following composition: NaCl 0,5 ‰, NaHCO₃ 0,2—0,285 ‰, CaCl₂·6 aq 0,04 ‰, KCl 0,01 ‰. Also for other organs of the frog the proper physiological fluid was found after systematical investigation (for the movements of the stomach on excitation of the N. vagus²⁾, for the movements of the rectum³⁾, for formation and solution of biliary concrements⁴⁾. All these researches have shown that the efficiency of the circulating fluid depends on the amount of free calcium-ions⁵⁾. Also in warm-blooded animals the concentration of Ca-ions appeared to play a prominent part: here we allude to the investigations on haemolysis⁶⁾ and on

¹⁾ H. J. HAMBURGER and R. BRINKMAN, These Proceedings Vol. XIX. p. 989 and Vol. XX, p. 668. See also Biochem. Zeitschr. 88, 97, 1918.

²⁾ BRINKMAN and VAN DAM, These Proc. 18 Dec. 1920.

³⁾ Demonstration by VAN CREVELD at the Conference of Physiologists at Amst. 22 Dec. 1921,

⁴⁾ BOLT and HEERES, Ned. Tijdschr. v. Geneesk. 65, 2d half N^o. 10, 1921. Also Pflüger's Archiv f. d. ges. Physiol. (not out yet).

⁵⁾ Cf. also H. J. HAMBURGER, Permeability in Physiology and Pathology, Lancet 2. 1055, 1921.

⁶⁾ BRINKMAN, Biochem. Zeitschr. 95, 101, 1919.

the origin of spasmophilic phenomena consequent on decrease of the concentration Ca-ions of the blood ¹⁾. This concentration depends upon Ca-ions the NaHCO_3 , and on the H-ion concentration.

As for the influence of the concentration of the Ca-ions upon the permeability of the glomerular epithelium, it is so great that, even when a *potassium-free* liquid is sent through the kidney, retention of the physiological quantity of glucose was still observable ²⁾.

This being the fact, it seemed interesting to us to investigate *with what liquid the vascular system of the frog had to be perfused in order to prevent the production of œdema in the hindlimb*.

We were all the more induced to inquire into this matter, since some years back GUNZBURG ³⁾ occupied himself with this question in the Utrecht Physiological Laboratory. He found that, when perfusing the vascular system of the frog with a fluid such as RINGER had used for the heart, and which differed from ours in NaHCO_3 0.02 % being used instead of 0.2 %—0.285 %, KCl 0.01 % was indispensable to prevent oedema. So, in GUNZBURG's experiments oedema arose when the fluid was potassium-free or when too large an amount of K was present. Instead of K he could use also Uranium, Thorium or Rubidium in definite quantities. It is evident, therefore, that, according to GUNZBURG, K is indispensable in this case, and this indispensability is, according to him, due to the specifically radio-active effect of this element.

But GUNZBURG also detected that in RINGER's mixture K could be left out, when the mixture was saturated with oxygen, in which case œdema was also prevented. We shall revert to this point.

It has been stated that in the circulating fluid HAMBURGER and BRINKMAN could do entirely without K. In that case, however, the Ca-ion concentration should have a definite value. The question now arose: *can œdema be prevented in the frog's limb with a potassium-free circulating fluid, the Ca-ions concentration being accurately fixed?*

In order to find an answer to this question we have a series of experiments which yielded unexpected results with reference to the influence of the Ca-ions concentration on the lumen of the blood-vessels (capillaries).

Of course the inquiry was begun by repeating GUNZBURG's experiments. A perfusion of the ordinary RINGER's liquid (NaHCO_3 0.02%)

¹⁾ VAN PAASSEN, Ned. Tijdschr. v. Geneesk. 65, 2e helft, nr. 17, 1921.

²⁾ HAMBURGER and BRINKMAN, These Proceedings Vol. XX, p. 668; Biochem. Zeitschr. 88, 97, 1918.

³⁾ GUNZBURG, Arch. Néerl. d. Physiol. 2, 364, 1918.

did not cause œdema, which indeed came forth, when K was left out, just as GUNZBURG has shown.

Now mixtures were applied of NaCl 0,6 % with several quanta of CaCl_2 . 6 aq. The result was that œdema appeared when CaCl_2 . 6 aq. 0,003 %, 0,005 %, 0,006 % was applied, but that *it stayed away when CaCl_2 . 6 aq. 0,007 %* was used, even when the hydrostatic pressure was raised from 35 to 70 cm.

These experiments, therefore, went to show that, contrary to GUNZBURG's opinion, K may be taken from the circulating fluid, without evoking œdema¹⁾, in other words, that *no radioactive substance is required* to prevent œdema.

Now it seemed to be interesting to add some K to this circulating fluid (NaCl 0,6 % + CaCl_2 . 6 aq. 0,007 %), which, as has been said, does not cause œdema. The addition of KCl 0,01 % produced œdema. It may be concluded, therefore, that *the absence of œdema on adding KCl in the experiments of GUNZBURG cannot be due to a specific Potassium-action*. On the other hand, it became rather evident, that when a definite concentration of it is present in our NaCl— CaCl_2 mixture, œdema is sure to appear on that account, so that it becomes obvious, that the prevention of œdema by the 0,007 % CaCl_2 . 6 aq. solution is balanced, and even more than balanced, (this depends on the amount) by the antagonistic Potassium.

Now, how are we to account for GUNZBURG's finding that a potassium-free RINGER's mixture evokes œdema? It is probably to be ascribed to the fact that this circulating fluid contained only 0,02% of NaHCO_3 , of which according to RONA and TAKAHASHI's²⁾ formula a large amount of Ca-ions is the consequence.

A direct measurement of the Ca-ions concentration after BRINKMAN and VAN DAM³⁾ proved that the Ca-ions concentration used by GUNZBURG was, indeed, much greater than in the above-named mixture of NaCl 0,6 % + CaCl_2 . 6 aq. 0,007 %.

We found experimentally that in our mixture NaCl- CaCl_2 , which did not bring about œdema, contained 13 mgrms of Ca-ions per Litre, whereas the liquid used by GUNZBURG contained 20 mgrs per Litre, which makes a difference of 35 %.

Now we know that K and Ca are antagonists; the action of K being liquifying, that of Ca tending towards coagulation. It is not

¹⁾ It has been shown that, with other kinds of frogs, there are sometimes other Ca-ion concentrations needed to prevent œdema.

²⁾ RONA u. TAKAHASHI, Biochem. Zeitschr. 49, 370, 1913.

³⁾ BRINKMAN and VAN DAM, These Proceedings, Vol. XXII, p. 762.

surprising, therefore, that the ratio of K- en Ca-ions is of great importance for the permeability of the vascular wall. It is evident that in an NaCl-CaCl₂ mixture the constricting power of 13 mgr. Ca-ions per Litre is so great, as to keep away œdema. In the presence of *more* than 13 mgr. Ca-ions e.g. 20 mgrs, as is the case in GUNZBURG's fluid, œdema will ensue, if not a certain amount of K is added to counteract their effect. A similar phenomenon appeared in the case of the kidneys viz. that an excess of Ca-ions content of the circulating fluid produced permeability of the glomerular epithelium for glucose ¹⁾. The same thing was found by BRINKMAN ²⁾ with regard to the red blood corpuscles. Likewise NEUSCHLOSZ ³⁾ physico-chemical experiments demonstrated that the surface-tension of a lecithin-suspension in NaCl is as well influenced in the same manner by too little as by too much Ca.

We now tried to ascertain, whether œdema would arise when using a mixture of NaCl—CaCl₂ which contained much more than 0,007 % of CaCl₂. 6 aq., just as had occurred when the amount was 0,006 %.

With a view to this 0.01 % CaCl₂ 6 aq. (instead of 0,007 %) was dissolved in NaCl 0.6 %. We expected œdema to come forth. It did not come forth, though, which was owing to a quite unexpected phenomenon: *the perfusion of the liquid through the vessels stopped abruptly*. It could not be restored even through a considerable rise of the hydrostatic pressure. When the same result was obtained several times running, also with higher Ca-ions concentrations ⁴⁾, further experiments concerning the influence of a higher Ca-ions concentration on the producing of œdema had to be relinquished, and vascular contraction was supposed to come into play.

Now the assumption was warrantable that the vascular contraction (spasm, tonus) would disappear on addition of K. It appeared, indeed *that when to the circulating fluid (NaCl 0,6% + CaCl₂ . 6 aq. 0.01 %) 0.01 % KCl was added the perfusion of the liquid was restored again*.

We are justified in concluding from this that when, in a system Na + Ca, the Ca-ions concentration is higher than agrees with CaCl₂ . 6 aq. 0.007 %, a constricting influence is exercised on the vessels, which may be counteracted by K-ions. This action seems to be reversible; it may be repeated several times.

¹⁾ HAMBURGER u. BRINKMAN, Biochem. Zeitschr. **95**, 101, 1919.

²⁾ R. BRINKMAN, Broch. Zeitschr. **95**, 101 (1919).

³⁾ NEUSCHLOSZ, Pflüger's Archiv f. d. ges. Physiol. **181**, 17, 1920.

⁴⁾ More about this in a subsequent publication.

In correlating this result with the well-known observations of CHIARI and JANUSCHKE¹⁾, according to which the process of conjunctival inflammation may be arrested by instillation of a CaCl_2 -solution, we are led to suppose that a definite concentration of Ca-ions exercises a constricting influence upon the vessels and at the same time a coagulating action upon the vascular wall. It appears then that both these actions are neutralised by K.

That the contracting and the coagulating action may coincide, is substantiated by the observations on the influence of oxygen. SÉVERINI²⁾ found that oxygen brings about contraction of the vessels; while GUNZBURG³⁾, reports that a potassium-free RINGER's mixture, which in other cases always caused œdema, did not cause it when the mixture was saturated with oxygen. From this it seems probable that *vascular contraction coincides with decrease of permeability of the vessel-wall* not only with a definite concentration of Ca-ions, but also under the influence of oxygen.

As regards the inhibition of vascular constriction through the addition of KCl to the mixture $\text{NaCl } 0,6\% + \text{CaCl}_2 \cdot 6 \text{ aq. } 0,01\%$, it appears that the minimal required concentration of KCl is about $\text{KCl } 0,004\%$.

S U M M A R Y.

The described researches, of which a detailed report appeared in the *Biochemische Zeitschrift*⁴⁾, may be summarized as follows:

1. When perfusing the frog's leg with an aqueous solution of NaCl and CaCl_2 , potassium may be absent in the circulating fluid, without œdema being evoked. The circulating fluid, however, should contain a definite concentration of calcium-ions. $\text{NaCl } 0,6\% \text{ CaCl}_2 \cdot 6 \text{ aq. } 0,007\%$, will serve our purpose here. When using $\text{CaCl}_2 \cdot 6 \text{ aq. } 0,006\%$, œdema will arise. This will occur also when to the first-named mixture $0,01\%$ KCl is added. This phenomenon finds an explanation in the fact that the coagulating action of the Ca-ions is counteracted by the antagonistic K-ions.

2. That GUNZBURG wanted potassium in his solution to prevent œdema is to be ascribed to the fact that he used an excess of calcium-ions. The arrest of œdema in GUNZBURG's experiments is,

¹⁾ CHIARI u. JANUSCHKE, Arch. f. exper. Pathol. u. Pharmakol. 65, 120-126, 1911.

²⁾ LUIGI SÉVERINI, „Ricerche sulla innervazione dei vasi sanguigni”. Perugia Boncompagni et Cie (See BAYLISS: „Principles of General Physiology”, 1915, p. 534.

³⁾ GUNZBURG, l.c.

⁴⁾ RUDOLF J. HAMBURGER, Bioch. Zeitschr. 129, 153, 1922.

therefore, *not owing to a specifically radio-active potassium-action* but only to the long known potassium-calcium antagonism.

3. The influence of the K-ion concentration upon the permeability of the vessel-wall (mentioned sub 1 and 2) coincides with an influence upon the capillary lumen. A perfusion of the vascular system of the frog with a mixture of NaCl 0.6 % + CaCl₂ . 6 aq 0.01 % produces so considerable a constriction of the vessels that no fluid can pass through any more. *When to this mixture a little KCl, say, 0.01 % KCl is added, the vessels dilate and the fluid runs on as before. This process is reversible.*

4. The parallelism of decrease of permeability and of constriction of the vessel-wall manifests itself not only under the influence of Ca-ions, but also under that of oxygen.

5. In a quantitative determination of the dilating and constricting action of pharmaca after TRENDELENBURG, due regard should be paid in future to the ratio of Potassium- and Calcium-ions in the circulating fluid.

*From the Physiological Laboratory of the
University of Groningen.*

5 March 1922.

ERRATUM.

In these Proceedings of June 1912 (Vol. XV), p. 276, Table II, column 5, line 12 from the bottom to replace the there printed number 1.18908 by the number **1.69487**.

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Physiology. — “*On the Alpha-automaticity of the Autonomous Organs.*” By Prof. H. ZWAARDEMAKER.

(Communicated at the meeting of June 24, 1922).

In the organism there are some organs which perform automatic movements and whose movements are continued also in parts that have been isolated from the body. Without any outward stimulation, simply by watching those parts we can follow up the continuation of this action in its causal and conditional relations. The type of such an organ is the heart. It is the musclecells themselves that pulsate, from the earliest embryonal existence up to death. Such a pulsating heart-cell is comparatively a simple system of phases,¹⁾ which, if the nucleus is left out of consideration, is made up of the following components: 1st. 7 ions, H, OH, Na, K, Ca, HCO₃, H₂PO₄ (resp. HPO₄); 2nd. 2 lipoids, cholesterin and lecithin; 3rd. a carbohydrate, glycogen, which is alternately combined with phosphoric acid and isolated from it again; 4th. oxygen; 5th. proteins and water as a solvent. The absolute quantity of every component exerts, according to the rules of the equilibrium of the phases, an influence upon the whole. Influence may be exerted, a component may even be given a certain concentration, by surrounding the cell with a nutrient liquid composed for the purpose. In so doing substitution appeared to be possible. Na may be replaced by Li or by highly purified Cs; K by all radio-active elements²⁾; Ca by Sr and Ba; lecithin by sodiumoleonate. Besides the absolute quantity also the mutual relations carry weight, notably H : OH, H : HCO₃, K : Ca. Such interrelations must keep within certain bounds. To test this various qualities of the function may be considered: first of all the so-called tonus-condition, i.e. the degree of continued contraction between the limits of atony and maximal tonus; next the excitability in the several intervals of a period; lastly the automatic movement itself. Now granting the conditions of the system to be so regulated that the bounds we alluded to, have been kept in view, and each

¹⁾ H. ZWAARDEMAKER, *Erg. des Physiol.* Bd. 5. p. 135. 1906.

²⁾ H. ZWAARDEMAKER, *These Proceedings* Vol. XIX, p. 633. (1916).

of the three fundamental manifestations, i.e. tonus, excitability and automaticity persist freely, two sorts of automaticity can be elicited by superadding successively the several radioactive elements to the nutrient liquid which surrounds the cells. Two sorts we say, because there are two groups of radio-active elements, which thus far I have been able to use as medium in the solutions of RINGER or TYRODE to substitute vice versa: 1st. an α -group: uranium, radium, emanation, polonium, thorium, 2nd a β -group: potassium, rubidium.

We shall now discuss the points of distinction and of agreement between these alpha-, and beta-automaticities.

The principal feature of an automatic, periodic movement is its tempo, which in its turn depends again on the so-called refractory stage inserted into every period. Now this tempo is determined by the amount of radio-activity for the alpha-group, as well as for the beta-group. A minimum amount is required for the movements to reveal themselves at all, and a maximum quantum that should on no account be surpassed. This allows a certain latitude for dosages, which is narrow for the alpha-, and broad for the beta-group.

Somewhere in this latitude there is a point of greatest frequency, the optimum. This point being established for the two sorts of rays, the frequencies will be the same for either group.

Such an investigation evidently requires a constant temperature. It is also clear that, when the temperature is variable the two determining factors: amount of radio-active matter and degree of the temperature, may cooperate or counteract each other. It has already been shown that there is a law, which determines these relations, but I do not intend to enter into it here. Now, when both for potassium and for uranium the optimum doses have been found, which yield the highest frequency, the frequencies for potassium- and for uranium-automaticity are equal. This is instanced in Fig. 1. In the centre the potassium-beat is shown, separated to the right and to the left by a standstill from two other pulsations; these two other pulsations represent the paradoxical phenomenon appearing when passing from perfect potassium-dosis to a perfect uranium-dosis, and conversely¹⁾. To the right and to the left the uranium-beat can be observed. Its frequency does not differ from that of the automaticity in the centre of the figure.

Another property the two automaticities have in common is a

¹⁾ These Proceedings Vol. XIX, p. 1043, (1917) C. R. Soc. de Biol. t. 84 p. 704. Paris 1921.

similar need for radio-activity in the several subdivisions of the heart. This is seen best when passing from a perfect uranium-dosis

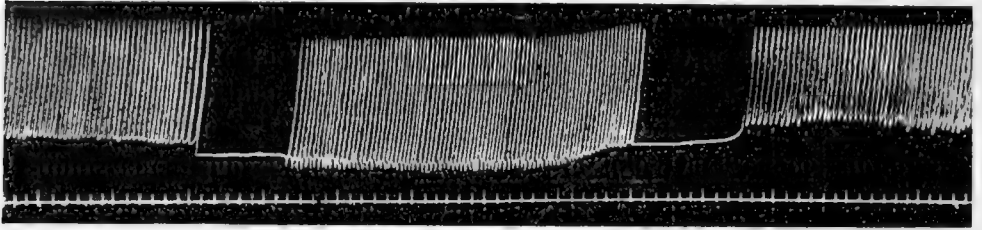


Fig. 1.

Frog's heart KRONECKER'S canula 14° C., red light.

Transition from a circulating fluid with 25 mgr. uranyl nitrate to another with 300 mgr. potassiumchlorid per litre, and then back again to 25 mgr. uranyl nitrate. The transitions generally took place resp. 40 and 60 seconds before the paradoxical standstills, indicated in the figure by a white line. Potassium pulsation in the centre. Time $\frac{1}{6}$ min.

to a perfect potassium-dosis or the reverse with a simultaneous registration of the sinus, atrium, ventricle. If no conductive disturbances occur, it will be seen that the three divisions of the heart will stand still and resume their beats at the same moment with automaticities of their own. This is illustrated below in fig. 2 for an eel-heart in situ, which was perfused first with a uranium-liquid and at a moment designated in the time-line by *S* with a potassium-liquid.

The phenomenon, instanced in fig. 2 requires, however, accurate dosage of uranium as well as of potassium. It would not be surprising, if inaccuracy in this respect should engender dromotropism.

A third property the two automaticities have in common is the self-regulation after extrasystole, for α -conditions as complete as for the β -conditions.

The fourth common property is the initial similarity of the alpha- and the beta-electrogram, though I must admit that afterwards a difference may come forth through secondary influences¹⁾.

Only in adventitious respects do the two automaticities differ.

Of the greatest importance in this respect is the tonicities of the heart. The conditions determining the auto-tonus of the cardiac muscle are:

¹⁾ Klinische Wochenschrift Jahrg. I N^o. 12 (or Diss. H. SLOOFF, Utrecht 4 July 1922).

- a. the number of calcium-ions placed or not placed over against univalent-ions.
- b. the number of H-ions.
- c. the amount of light incident upon the heart, especially in the presence of a fluorescent substance.

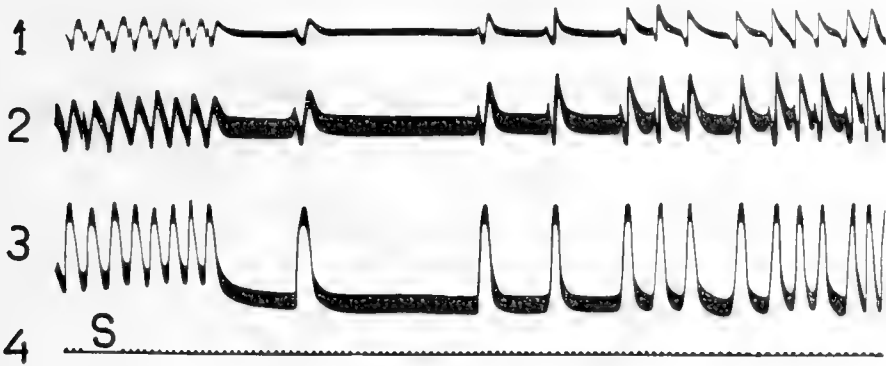


Fig. 2.

Eel's heart in situ. Perfusion from vena cava, first with a circulating fluid, containing 15 mgr. thorium-nitrate per litre, then with a circulating fluid, containing 100 mgr potassium-nitrate. 1 sinus, 2 atrium, 3 ventricle. Time in sec. At S transition from one fluid (thorium-beat) to the other (potassium-beat). Only in the ventricle a light tonus is noticeable during the thorium-beat. It has disappeared already for the greater part in the first beat performed by the heart during the paradoxon.

When applying uranium as an α -rayer each of the three above conditions is modified. Sub *a* undergoes a change because over against the calcium-ion not only univalent ions are placed, but also uranyl. Sub *b* is modified, because a solution of uranyl-salt causes a small increase of H-ions in Ringer's solution. True, this factor may be eliminated by the addition of a trace of CaCO_3 , but let it be supposed that this did not take place. Sub *c* has been modified, because in the organ perfused with a potassium-fluid the incident light has only an inappreciable influence unless its strength be enormous, while in the presence of a fluorescent uranium-liquid also ordinary light will show its tonic action.

It will, therefore, be considered quite rational that in fig. 1 the bases of the uranium-elevations are not so low as those of the potassium-elevations. When thorium is substituted for uranium the phenomenon is less pronounced, still, it is certain that even then the tonus is not quite absent.

With emanation-beats¹⁾ and with pulsation evoked by outside radiations with polonium, there is often some increase of tonus,

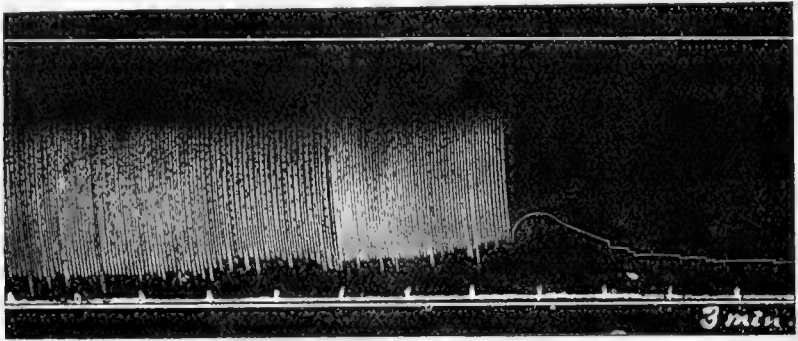


Fig. 3.

Frog's heart, KRONECKER'S cannula.

Deprived for some hours by potassium-free perfusion of diffusing potassium and of part of the depot. Then pulsating during the night with 100 mgr. of potassium-chlorid per litre. Next morning standstill with potassium-free Ringer's mixture. Recovery of pulsation due to omnilateral polonium-radiation. At the beginning of the curve the polonium was taken away.

Nearly half an hour later the polonium-beats cease. They had caused no increase of tonus worth mentioning.

which need not surprise us if we consider what has been stated sub *a*. Increase of tonus, however, is not a typical feature of alpha-automaticity, since it can exist without this increase when it is brought about from the outside by polonium-radiation. This is illustrated in Fig. 3²⁾. A heart that after cautious, prolonged perfusion with potassium-free Ringer's solution, had been deprived of a considerable portion of its potassium depot, continued pulsating for a long time also when subjected from the outside to omnilateral polonium-radiation. These pulsations occur without additional increase of tonus. The polonium is taken away at the beginning of the figure.

Besides in the tonus-condition, the two automaticities are also distinguished in the relation of the regularly pulsating hearts to the action of the constant current, to the alternating current and to diathermy. These distinctions have been described by Dr. DEN BOER³⁾ in his Thesis, so that I will not revert to them.

¹⁾ ZWAARDEMAKER and T. P. FEENSTRA, C. R. Soc. de biologie, t. 84, p. 377. Paris 1921. ZWAARDEMAKER, Klin. Wochenschr. Jahrg. I, N^o. 11. 1922. Arch. intern. de Physiol. vol. 18, p. 284, 1921.

²⁾ Another instance is given by ZWAARDEMAKER and G. GRIJNS, Arch. néerland. de physiol. t. 2, p. 502, 1918.

³⁾ M. DEN BOER, Dissertation. Utrecht 1 Maart 1921.

The heart has served us as a type of the two automaticities; the natural one depending on the radio-activity of potassium, or rubidium, and the artificial one, that can be evoked by the radio-activity of uranium, thorium, ionium, radium, emanation. In quite the same way there is a mutual resemblance between the alpha- and beta-automaticities of the gut and the uterus.

Botany. — “*Further researches on the antiphototropic curvatures occurring in the coleoptiles of Avena.*” By Dr. C. E. B. BREMEKAMP. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of May 27, 1922).

As I have shown in my former communication¹⁾, the conditions under which the coleoptiles of *Avena* produce an antiphototropic curvature, may be summed up in this way:

1st. At the end of the one-sided illumination the rate of growth should have about the same value at both sides of the coleoptile²⁾. This result is only to be obtained with light of rather strong intensity. If this is provided for, the product of the intensity and the exposition-time should exceed a certain value.

2nd. After the close of the illumination, there should be a more rapid increase of the growth-rate, in the side that has received the greatest quantity of light. In this way it should reach here a higher value.

An explanation of the way wherein a difference in the rate of increase may come about, was given in my paper entitled: “*Theorie des Phototropismus*”³⁾. After a previous diminution in consequence of the illumination, the rate of growth after some time increases again. This process commences probably the sooner, according as the diminution has been the greater. In this way the increase of the growth-rate in the side which has received the greatest quantity

¹⁾ C. E. B. BREMEKAMP. On antiphototropic curvatures occurring in the coleoptiles of *Avena*. Proceedings Kon. Akad. v. Wetensch. te Amsterdam. Vol. XXIV, p. 177. 1921.

²⁾ In my previous work in stead of the expression “the rate of growth at the end of the illumination” I used the ampler expression “the rate of growth belonging to the grade of sensibility existing at the end of the illumination”. In this way I reckoned with the possibility that it would give a latent period between the phototropic reaction i.e. the change of the rate of growth and the absorption of the light with its influence on the sensibility. However, a critical examination of the literature on this subject, has convinced me that the evidence in favour of the existence of this latent period, is not conclusive. The investigations of Bose and others have made it very probable that the reaction follows the illumination almost immediately.

³⁾ C. E. B. BREMEKAMP. *Theorie des Phototropismus*. Rec. d. trav. bot. Néerlandais Vol. XV, p. 123. 1918.

of light, may gain an advantage of that in the other side. This advantage will be the greater, according as there lies more time between the moment whereon the growth-rate in the anterior side has reached its lowest value, and the moment whereon this is the case in the posterior side. If it is sufficiently great, the rate of growth in the first-named side with the aid of it will reach at the end of the illumination or shortly afterwards a higher value. In any case the exposition-time should be long enough that an advantage of sufficient extent may be gained.

However, in my previous communication I showed that an anti-phototropic curvature may come about also, if the exposition-time is very short. As in this case the explanation given above naturally fails, I suggested that the theory of BOSE¹⁾ might give us here the clue to get out of the difficulty.

According to this theory, a disturbance of equilibrium in the organism generally manifests itself in a local contraction (the direct effect) which is accompanied by an expansion in the adjoining tissue (the indirect effect). In the latter, the turgescence would be heightened by the water expelled from the contracted portion, and accordingly a temporary enhancement of the growth-rate would be the result. In this way a normal curvature in one part of an organ would always go together with an antitropic one in the adjoining region. Only if an increase of the rate of growth in that part, should be impossible, the antitropic curvature would remain out. In our case then, the origin of the antiphototropic curvature in the tip of the coleoptile might be connected with the origin of a normal phototropic curvature in the basal part.

To test the correctness of this supposition, I made a number of experiments wherein the phototropic reaction of coleoptiles exposed in the whole of their length, was compared with the reaction of coleoptiles illuminated at the tip only, or illuminated also in the whole of their length, but after an exposition of the basal part to a two-sided illumination of rather great strength.

Before I enter into the details of these experiments, I will give a survey of the results which previous investigators have obtained in their researches on the influence of an illumination of one part, on the phototropic reaction of another.

First of all then, we have to consider the experiments on phototropism made by BOSE²⁾ himself. They are rather few in number,

¹⁾ J. C. BOSE. *Plant Respose*. London 1906.

²⁾ J. C. BOSE assisted by Jyotiprakash Sircar. The transmitted effect of photic stimulation. *Life Movements in Plants*. Calcutta 1918/19. p. 362—377.

and form only a subordinate part in the general frame of his work. His experimental objects were seedlings of *Setaria* and roots of *Sinapis*.

The choice of the first-named object is not very happy, as the direct effect of the exposition of the coleoptile is not outwardly visible, and its existence therefore, as yet purely hypothetical. The indirect effect consists in an antitropic curvature of the axis. This curvature which appears almost immediately, is followed in about 25 minutes by a normal one. The latter should be the result of the propagation of the invisible direct effect. An illumination of the growing region gives a normal curvature.

That the antitropic curvature of the axis occurring with an exposition of the coleoptile should be the indirect effect of this illumination in the sense of Bose, is possible. It should be remarked however, that it is not proved. As yet, we don't know with certainty, if in this case the direct effect consists really in a contraction, as no sign thereof becomes outwardly visible.

The roots of *Sinapis* show a negative phototropism. At least this is the case, when both the tip and the growing region are exposed to the light. The curvature appears in the growing region, the tip always remaining straight. An exposition of the tip also gives a negative curvature of the growing region, but if this part itself is exposed to the light, there appears at first a positive curvature which only after some time is followed by a weak negative one.

Bose considers the negative curvature in the growing region produced by an exposition of the tip, as the indirect effect, the direct effect as in *Setaria* remaining concealed. That this curvature is not, as in *Setaria*, followed by a positive one, he explains by assuming that the intervening tissue would be practically unable to conduct the direct effect. In the case of an exposition of the growing region, the positive curvature is considered as the direct effect, whereas the negative curvature appearing a little later, is said to arise on account of transverse conduction of the direct effect under continued illumination.

However, this explanation is not very convincing. That a neutralisation of the curvature might come about by transverse conduction, is quite conceivable; but how a reversion of the curvature might be explained in this way, I fail to understand. Moreover, as a conductivity for the direct effect in the longitudinal direction is supposed to be absent, it is not readily admissible that it should be very efficacious in the transverse direction. Therefore, in this case the interpretation of Bose cannot be considered as sufficiently founded.

The explanations of these negative curvatures given by other investigators are, however, hardly more convincing.

Information about the influence of an illumination of the basal part on the reaction of the tip, is to be found in papers by VAN DER WOLK ¹⁾, GUTTENBERG ²⁾ and ARISZ ³⁾, all dealing with the phototropism of *Avena*.

According to VAN DER WOLK the results of an illumination of the basal half of the coleoptile on the upper half, is to be seen in the fact, that an illumination of 12 MCS gives in these seedlings a curvature of the same strength as an illumination of 85 MCS in a wholly etiolated coleoptile. This greater curvability of the upper half might, perhaps, be explained by assuming that the contraction of the tissue in this part was facilitated by the decrease of turgescence in the basal half: the expulsion of the water would find here less resistance.

GUTTENBERG on the contrary, tried to show, that the curvability of the tip of the coleoptile is not altered by an illumination of the basal part. In his experiments three sets of seedlings were compared. They were all illuminated unilaterally with 22,2 or 33,3 MCS; but in the second and third set the basal part was exposed previously during one hour to an illumination with 11,1 MC; in the second set the seedlings rotated during this time round a vertical axis, whereas in the third set they stood still. In this case the after-illumination took place from the opposite side. GUTTENBERG found that the phototropic curvature in the third set was a little weaker than in the other two.

This result seems at first in flagrant contradiction to the statement of VAN DER WOLK cited above, but it should be remembered that in the experiments of VAN DER WOLK, the light was very strong, and the exposition only short, whereas GUTTENBERG used light of rather feeble intensity and a very long exposition. Therefore, in the seedlings of VAN DER WOLK the decrease of turgescence in the basal part, might have been greater, and consequently the effect on the curvability of the tip more important than in the seedlings of GUTTENBERG. This explanation would probably suffice, if there was no difference at all between the curvatures in the three sets. GUT-

¹⁾ P. C. VAN DER WOLK. Investigations of the transmission of light stimuli in the seedlings of *Avena*. These Proceedings, Vol. XIV, p. 327.

²⁾ H RITTER VON GUTTENBERG. Ueber akropetale Reizleitung. Jhrb. f. wis. Bot. Bd. 52 p. 333. 1913.

³⁾ W. H. ARISZ. Untersuchungen über den Phototropismus. Rec. d trav. bot. Néerlandais. Vol. XII p. 44. 1915.

TENBERG stated however, that the curvature in the third set was smaller than in the other two, and explained this discrepancy by assuming a propagation of the basal curvature to the tip. In my opinion it might have its cause in the circumstance, that these seedlings were already slightly curved at the moment of the after-illumination. If this had been the case, the tip would have received here a smaller quantity of light and this moreover partly under a less favourable angle than in the other sets, and consequently, the phototropic curvature would not have attained the same value. It should also be mentioned, that a repetition of these experiments by ARISZ (l.c. p. 105) gave only doubtful results, the sources of error being very great. In any case, we dare not say, that the acropetal propagation of the basal curvature has been demonstrated, and for the solution of the question, whether an exposition of the basal part exercises any influence on the curvability of the tip, the experiments are not suitable, the intensity of the light being too weak.

Nevertheless, there are in the paper of GUTTENBERG a few indications, which seem to show that the illumination of the basal part influences the curvability of the tip, in the way described by VAN DER WOLK. On p. 341 one may read: "Ein deutlicher Unterschied zwischen den Krümmungswinkeln der beiden Serien war dabei nicht zu konstatieren; doch verhielten sich die allseits vorbeleuchteten Pflanzen zunächst etwas anders als die verdunkelten. Bei ersteren erfährt nämlich das oberste Drittel der Koleoptile eine etwas stärkere Krümmung als bei letzteren, dafür ist aber bei diesen die Krümmung bereits weiter nach unten fortgeschritten". That these differences were only very small (further data l.c. p. 437) and quantitatively very different from those observed by VAN DER WOLK, may find its explanation, as I have pointed out already, in the feeble intensity of GUTTENBERG's illumination.

ARISZ mentions (l. c. p. 103), that he has repeated the experiments of VAN DER WOLK, and describes his results in this way: „Wohl ist in vielen Fällen eine kleine Vergrößerung der Spitzenkrümmung beobachtet worden, welche auch etwas früher sichtbar wurde, aber so eklatant, wie VAN DER WOLK seine Resultate beschreibt, war es nicht". ARISZ therefore does not deny, that the illumination of the basal part enhances the curvability of the tip; only he awards this influence less importance than VAN DER WOLK does.

Summing up, we may state that our knowledge of the influence which an exposition of the basal part exercises on the tip, is far from complete. Moreover, it cannot be said that the available data

are very valuable for our supposition, that the antiphototropic curvatures of *Avena* might find their explanation in this way.

In the experiments of ARISZ (l.c. p. 97), the exposition of the basal part gave a normal curvature¹⁾, which did not extend itself beyond the limits of the part exposed. As the occurrence of an antiphototropic curvature in the tip is never mentioned, we must assume that under the circumstances of these experiments, the tip remained perfectly straight. At first sight, this seems to clash with our supposition, but we should remember, that in these experiments the tip remained continually in the dark, so that its turgescence underwent no decrease. Now in consequence of this circumstance, an increase of the rate of growth might be difficult or even impossible.

In my own experiments I compared in the first place the reaction of coleoptiles exposed at the tip only, with the reaction of coleoptiles exposed in the whole of their length. The result was very clear. Whereas in the first case antitropic curvatures were never found, in the second case they could be obtained without difficulty.

The etiolated seedlings used for these experiments, were planted in a single row in oblong zinc boxes. Each box got about 15 seedlings, so orientated, that their plane of symmetry was parallel to the small side of the box. During the exposition, the boxes were placed perpendicular to the rays of light. The seedlings that should be exposed at the tip only, stood with their basal part behind a screen, so that only $2\frac{1}{2}$ —3 mm. of the tip protruded. This screen was prepared in the following way. A feeble red light was placed just in front of the experimental lamp, and the silhouette of the coleoptiles caught on a piece of black paste-board standing just behind them. The place of the tip was marked thereon with the aid of a pencil. Above these marks the paste-board was cut away and then the screen pushed $2\frac{1}{2}$ —3 mm. deeper in the earth. After that the box was turned round and the red light removed. During the illumination with the experimental lamp, in this way just $2\frac{1}{2}$ —3 mm. of the tip was exposed.

The intensity of the illumination was in all experiments 750 MC;

¹⁾ In two experiments out of a very great number, ARISZ mentions to have obtained antitropic curvatures in the part exposed. In one case (illumination during 1 minute with 330 MC), the curvatures are stated to have been feebly normal or antitropic, in the other case (illumination during 1 minute with 200 MC), they were antitropic or absent. As these cases, however, stand wholly isolated among the rest of his results, it seems probable that these antitropic curvatures are due to some experimental error.

the exposition-time 12, 15, 18 and 21 seconds. The temperature varied between 15° and 20° C., but in each series of experiments it remained nearly constant. After the illumination the boxes came on the clinostat.

With an exposition of 12 seconds (light-quantity 9000 MCS), after 3½ hours the coleoptiles exposed in the whole of their length, were feebly antitropic (S-shaped); the coleoptiles exposed at the tip only, feebly curved in the normal way.

With an exposition of 15 seconds (light-quantity 11250 MCS), the results were nearly the same.

With an exposition of 18 seconds (light-quantity 13500 MCS), after 3½ hours the coleoptiles exposed totally, were clearly antitropic (feebly S-shaped), the coleoptiles exposed at the tip only, nearly straight.

With an exposition of 21 seconds (light-quantity 15750 MCS), after 3½ hours the coleoptiles were all nearly straight.

The experiment with the exposition-time of 15 seconds, was repeated 5 times, always with the same result. That in this case, the occurrence of an antitropic curvature at the tip of the totally exposed coleoptiles, is dependant upon the exposition of the basal part, cannot be doubted.

The results of the experiments wherein the basal part of the coleoptiles was previously exposed to a very strong illumination, and where, therefore, the unilateral after-illumination of the whole coleoptile did not give a normal curvature in the basal part, demonstrate the significance of this influence also clearly.

In these experiments, I compared the result of an unilateral illumination of the whole coleoptile after a twosided exposition of the basal part, with that of an unilateral illumination of seedlings previously kept in the dark. During the fore-illumination two screens of the same shape were used, one in front of the coleoptiles, and one behind them. They were prepared in the same way as those used in the previous experiments, the only difference being that in this case, the basal part of the paste-board was for the greater part cut away. In this way during the illumination, at the tip of the coleoptiles a piece of 2½—3 mm. remained in the dark. The fore-illumination lasted 60 seconds, and during this time, every 10 seconds the box was turned round. At the end of the fore-illumination the box was turned round for the last time, then the screens were taken away, and the seedlings once more exposed to the same light. This time the illumination lasted 12 or 15 seconds. The intensity of the illumination was always 750 MC. The result of these experiments

was, that the coleoptiles, whereof the basal part was previously exposed, remained straight, whereas the others showed the usual antiphototropic curvature.

In my former communication I admitted that in coleoptiles previously submitted to an omnilateral illumination of a definite value, an antiphototropic curvature might, perhaps, be obtained with the aid of a rather weak after-illumination. This seems now not very probable, as under these circumstances, the occurrence of a normal curvature in the basal part, may hardly be expected. Therefore, in this case neither of the causes hitherto discovered, by which an antiphototropic curvature may be produced, is present.

The relative importance of the two causes is as yet wholly unknown, but that the cause discussed in this paper, must be very efficient, follows from the experiments described in my former communication (l.c. p. 182). The antiphototropic curvatures produced by an illumination with a given quantity of light, showed but little difference if the exposition-time varied between 1 and 256 or between $\frac{3}{4}$ and 192 seconds. Now, as we have seen that with a very short exposition-time, the presence of the cause discussed in my earlier work, is wholly excluded, we must conclude that its influence in the experiments with a longer exposition, was here also rather weak.

S U M M A R Y.

The antiphototropic curvature which appears at the tip of the coleoptile of *Avena* with a very short exposition, does not show itself, if the illumination is limited to the tip, or if the basal part has previously been exposed to a rather strong illumination.

Therefore we should assume, that with an unilateral illumination of the whole coleoptile, the rate of growth of the tip, is enhanced by an influence proceeding from the basal part. This influence must be greatest in the side, which underwent the greatest contraction, that is to say in the side, which during the exposition faced the lamp. The origin of an antiphototropic curvature of this kind is, therefore, always connected with the origin of a normal curvature in the basal part.

Mathematics. — „*Ueber Wirkungsfunctionen*“. By Prof. R. WEITZENBÖCK. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of May 27, 1922.)

§ 1. *Einleitung.*

Bei der Ableitung der Feldgesetze und der Erhaltungssätze in der allgemeinen Relativitätstheorie und deren Erweiterungen steht man vor folgender Aufgabe: wenn g_{ik} und φ_i die Komponenten eines Kovarianten Tensors. 2. resp. 1. Stufe sind und

$$g_{ik,\alpha} = \frac{\partial g_{ik}}{\partial x_\alpha}, \quad g_{ik,\alpha\beta} = \frac{\partial^2 g_{ik}}{\partial x_\alpha \partial x_\beta}, \quad \varphi_{i,\alpha} = \frac{\partial \varphi_i}{\partial x_\alpha}, \quad \varphi_{i,\alpha\beta} = \frac{\partial^2 \varphi_i}{\partial x_\alpha \partial x_\beta} \quad . \quad (1)$$

gesetzt wird, so ist aus diesen Funktionen eine absolute Invariante W zu bilden. $W\sqrt{g}$ wird dann eine relative Differentialinvariante vom Gewichte eins (= eine scalare Dichte) und

$$\int \mathfrak{B} \, dx = \int W \sqrt{g} \, dx = \iiint \int W \sqrt{g} \, dx_1 \, dx_2 \, dx_3 \, dx_4 \quad . \quad (2)$$

wird eine absolute Integralinvariante.

Man nennt \mathfrak{B} die Wirkungsfunction. Bedeutet δ eine Variation der g_{ik} und φ_i , so gibt die Gleichung

$$\delta \int \mathfrak{B} \, dx = 0 \quad (\text{für alle } \delta g_{ik} \text{ und } \delta \varphi_i) \quad . \quad . \quad . \quad (3)$$

die Feldgesetze.

Die Frage nach allen Differentialinvarianten zweiter Ordnung der beiden Tensoren g_{ik} und φ_i wird zurückgeführt auf die einfachere Frage nach allen ganzen, rationalen Differentialinvarianten dieser Tensoren. Hierauf gibt ein Reduktionssatz von RICCI und LEVI-CIVITÀ¹⁾ die Antwort: man hat alle projektiven Invarianten der folgenden 5 Tensoren zu suchen!

$$\left. \begin{aligned} g_{ik} &= \text{metrischer Fundamentaltensor} \\ \varphi_i &= \text{electromagnetisches Potential} \\ R_{ik,\alpha\beta} &= (\text{Riemann-Christoffel'scher}) \text{ Krümmungstensor} \\ \varphi_{i(\alpha} &= \text{erste kovariante Ableitung der } \varphi_i \\ \varphi_{i(\alpha)\beta)} &= \text{zweite kovariante Ableitung der } \varphi_i. \end{aligned} \right\} \quad . \quad (4)$$

¹⁾ Mathem. Ann. 54, (1901), p. 138.

Die Frage nach *allen* projektiven Invarianten dieser Tensoren bildet ein sehr kompliziertes algebraisches Problem. (Nach dem allgemeinen Endlichkeitssatz von HILBERT gibt es *endlich-viele* ganze rationale Invarianten, durch die sich alle übrigen ganz und rational ausdrücken lassen.)

Glücklicherweise ist hier die Sache nicht so trostlos verwickelt, indem zwei sehr einschränkende Forderungen gestellt werden: in der EINSTEIN'schen Theorie wird verlangt, dass die Feldgesetze Differentialgleichungen höchstens zweiter Ordnung werden; in der Theorie von WEYL müssen die aus den Tensoren (4) gebildeten Wirkungsfunktionen auch masstabsinvariant sein.

Wir behandeln zuerst den zweiten Fall.

§ 2. Die Theorie von WEYL.

In der durch WEYL gegebenen Erweiterung der allgemeiner Relativitätstheorie muss die aus den Tensoren (4) gebildete Wirkungsfunktion absolut-invariant gegenüber Masstabtransformationen sein. Diese Transformationen sind gegeben durch

$$g'_{ik} = \lambda g_{ik} \quad \varphi'_i = \varphi_i - \frac{\partial \log \lambda}{\partial x_i}, \quad . \quad . \quad . \quad (5)$$

woraus noch entsprechende Gleichungen für $R'_{ik,\alpha\beta}$, $\varphi'_{i(\alpha)}$ und $\varphi'_{i(\alpha)(\beta)}$ folgen.

Die Forderung $\mathfrak{B}' = \mathfrak{B}$ (für alle λ) erniedrigt dann die Anzahl 5 der Tensoren (4) auf 4 masstabinvariante Tensoren:

$$\left. \begin{aligned} g_{ik} &= \text{metrischer Fundamentaltensor} & (g'_{ik} = \lambda g_{ik}) \\ f_{ik} &= \text{electromagnetisches Feld} & (f'_{ik} = f_{ik}) \\ *F_{ik,\alpha\beta} &= \text{Richtungskrümmung} & (*F'_{ik,\alpha\beta} = \lambda *F_{ik,\alpha\beta}) \\ E_{ik,\alpha} &= f_{i(\alpha)\beta} - \frac{1}{2}(f_{\alpha k} \varphi_i + f_{i\alpha} \varphi_k + 2f_{ik} \varphi_\alpha - g_{\alpha i} f_{\beta k} \varphi^\beta - g_{\alpha k} f_{i\beta} \varphi^\beta) & (E'_{ik,\alpha} = E_{ik,\alpha}) \end{aligned} \right\} \cdot (6)$$

Der gegenüber $\mathfrak{B} = WV/g$ etwas allgemeinere Ansatz $\mathfrak{B} = Wg^h$, wobei W keinen Faktor g mehr enthält, führt weiters auf die Gleichung

$$2n_2 + 2n_3 + 3n_4 = 4,$$

wobei W ganz und rational vom Grade n_2, n_3, n_4 in den f_{ik} , $*F_{ik,\alpha\beta}$ und $E_{ik,\alpha}$ ist. Daher ist $n_4 = 0$ und für n_2 und n_3 bleiben nur die drei Möglichkeiten (2,0), (1,1) und (0,2) übrig. Man kann dann beweisen¹⁾, dass sich unter diesen Annahmen nur die folgenden sechs Wirkungsfunktionen ergeben:

¹⁾ R. WEITZENBÖCK, Wiener Ber. 129, (1920), p. 683 und p. 697; dito, 130, (1921), p. 15.

$$\begin{aligned}
 \mathfrak{B}_1 &= \sum_{ik} f_{ik} f_{i'k'} = 2(f_{12} f_{34} + f_{13} f_{42} + f_{14} f_{23}) \\
 \mathfrak{B}_2 &= f_{ik} f^{ik} \sqrt{g} \\
 \mathfrak{B}_3 &= \frac{1}{\sqrt{g}} \sum_{ik} \sum_{lm} *F_{ik,lm} *F_{i'k',l'm'} \\
 \mathfrak{B}_4 &= \sum_{ik} *F_{ik,00}^{00,ik} *F_{i'k',\lambda\mu} \\
 \mathfrak{B}_5 &= (*F_{ik,00}^{00,ik})^2 \sqrt{g} \\
 \mathfrak{B}_6 &= *F_{ik,lm} *F_{i'k',lm} \sqrt{g}
 \end{aligned} \quad \left. \begin{array}{l} \\ \\ \\ \\ \\ \end{array} \right\} \dots \dots (7)$$

Hiezu machen wir die folgenden Bemerkungen¹⁾. \mathfrak{B}_1 und \mathfrak{B}_4 kommen als Wirkingsfunktionen nicht in Betracht, da ihre Variationen identisch Null geben, wie R. BACH bewiesen hat²⁾. \mathfrak{B}_2 ist die MAXWELL'sche Wirkingsfunktion, bei WEYL mit 1 bezeichnet³⁾. Auch $\mathfrak{B}_5 = L^2 \sqrt{g}$ wird von WEYL verwendet.

An Stelle von \mathfrak{B}_3 kann man auch die Invariante

$$W_3' = *F_{ik} *F^{ik} \quad , \quad \mathfrak{B}_3' = W_3' \sqrt{g} \quad \dots \dots (8)$$

verwenden; es ist nämlich:

$$\mathfrak{B}_3 = -\mathfrak{B}_3' + \frac{1}{4} \mathfrak{B}_2 + \frac{1}{4} \mathfrak{B}_5 + \mathfrak{B}_6 \quad \dots \dots (9)$$

Die Variationen von \mathfrak{B}_3' und \mathfrak{B}_6 wurden von W. PAULI⁴⁾ und R. BACH²⁾ berechnet.

§ 3. Die Theorie von EINSTEIN.

In der EINSTEIN'schen Theorie ist $\mathfrak{B} = W \sqrt{g}$ und W ist aus den Tensoren (4) zusammen gesetzt: rational in den g_{ik} , ganz und rational in den übrigen vier Tensoren.

Variieren wir die g_{ik} allein, so bekommen wir die Gravitationsgleichungen $\mathfrak{B}^{ik} = 0$; die Variation von φ_i ergibt die verallgemeinerten MAXWELL'schen Gleichungen $w_i = 0$. Dabei sind diese „Tensor-dichten“⁵⁾ gegeben durch:

$$\mathfrak{B}^{ik} = \frac{\partial \mathfrak{B}}{\partial g_{ik}} - \frac{\partial}{\partial x_\alpha} \left(\frac{\partial \mathfrak{B}}{\partial g_{ik, \alpha}} \right) + \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \left(\frac{\partial \mathfrak{B}}{\partial g_{ik, \alpha\beta}} \right) \quad \dots \dots (10)$$

$$w_i = \frac{\partial \mathfrak{B}}{\partial \varphi_i} - \frac{\partial}{\partial x_\alpha} \left(\frac{\partial \mathfrak{B}}{\partial \varphi_{i, \alpha}} \right) + \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \left(\frac{\partial \mathfrak{B}}{\partial \varphi_{i, \alpha\beta}} \right) \quad \dots \dots (11)$$

¹⁾ H. WEYL, Phys. Zeitschr., 22, (1921), p. 473.

²⁾ R. BACH, Mathem. Zeitschr. 9, (1921), p. 124.

³⁾ H. WEYL, Raum, Zeit, Materie, 4. Aufl., (1921), p. 268.

⁴⁾ W. PAULI, Phys. Zeitschr., 20, (1919), p. 457; Verhdl. d. Deutsch. Phys. Ges. 21, (1919), p. 742.

⁵⁾ D. HILBERT, Göttinger Nachr. 20. 11. 1915.

R. WEITZENBÖCK, Wiener Ber. 130, (1921), p. 15.

Berechnet man diese „Variations-Ableitungen“ und verlangt man, dass sie Differentialquotienten von höchstens zweiter Ordnung enthalten, so ergeben sich die drei folgenden Möglichkeiten:

A. W enthält die $R_{ik,\alpha\beta}$ linear, keine $\varphi_{i(\alpha)}$ und keine $\varphi_{i(\alpha)(\beta)}$:

$$W = A(g_{ik}, \varphi_i, R_{ik,\alpha\beta}); \dots \dots \dots (12)$$

B. W enthält die $\varphi_{i(\alpha)(\beta)}$ linear, keine $R_{ik,\alpha\beta}$ und keine $\varphi_{i(\alpha)}$:

$$W = B(g_{ik}, \varphi_i, \varphi_{i(\alpha)(\beta)}); \dots \dots \dots (13)$$

C. W enthält keine $R_{ik,\alpha\beta}$ und keine $\varphi_{i(\alpha)(\beta)}$:

$$W = C(g_{ik}, \varphi_i, \varphi_{i(\alpha)}). \dots \dots \dots (14)$$

Wir behandeln diese drei Fälle der Reihe nach. Bei A kann man zeigen, dass man nur die zwei Invarianten erhält:

$$A_1 = R = g^{ik} R_{ik}, \quad A_2 = R_{ik} \varphi^i \varphi^k \dots \dots \dots (15)$$

A_1 ist das von EINSTEIN verwendete R .

Im Falle B haben wir drei Invarianten:

$$B_1 = \varphi_{o(x)(i)}^i \varphi^\alpha, \quad B_2 = \varphi_{io(x)}^{o\alpha o} \varphi^i, \quad B_3 = \varphi_{i(\alpha)(\beta)} \varphi^i \varphi^\alpha \varphi^\beta. (16)$$

Die neben B_1 noch mögliche Invariante

$$B'_1 = \varphi_{o(\tilde{i})(\alpha)}^i \varphi^\alpha$$

ist mit Hilfe von B_1 und A_2 ausdrückbar:

$$B_1 - B'_1 = \varphi_{o(x)(i)}^i \varphi^\alpha - \varphi_{o(i)(\alpha)}^i \varphi^\alpha = -R_{\alpha\beta} \varphi^\alpha \varphi^\beta = -A_2 (17)$$

Komplizierter ist der dritte Fall C. Hier ist die Anzahl der Invarianten sehr gross: das Aufsuchen aller Invarianten kommt hinaus auf das Berechnen eines vollen Systems von orthogonalen Invarianten einer quaternären Linearform φ_i und einer ebensolchen (unsymmetrischen) Bilinearform $\varphi_{i(\alpha)}$. Dies ist eine bisher noch ungelöste Aufgabe.

Wir führen einige der einfachsten Invarianten vom Typus C an. Enthält C erstens keine $\varphi_{i(\alpha)}$, so haben wir die einzige Invariante

$$C_1 = \varphi = \varphi_i \varphi^i = g^{ik} \varphi_i \varphi_k \dots \dots \dots (18)$$

Wenn C die $\varphi_{i(\alpha)}$ linear enthält, haben wir zwei Invarianten

$$C_2 = \varphi_{i(\alpha)} \varphi^i \varphi^\alpha, \quad C_3 = \varphi_{o(i)}^i = \frac{1}{\sqrt{g}} \frac{\partial (\varphi^i \sqrt{g})}{\partial x_i} \dots \dots (19)$$

Die Wirkungsfunktion $C_3 \sqrt{g}$ gibt zu den Feldgesetzen keinen Beitrag, da $C_3 \sqrt{g}$ eine Divergenz ist.

Von den in den $\varphi_{i(\alpha)}$ quadratischen Invarianten C nennen wir nur noch

$$C_4 = 2 (\varphi_{i(\alpha)} \varphi^{i(\alpha)} - \varphi_{i(\alpha)} \varphi^{\alpha(i)}) = f_{ik} f^{ik}; \dots \dots \dots (20)$$

Hier ist f_{ik} das elektromagnetische Feld und $C_4 \sqrt{g}$ ist die MAXWELL'sche Wirkungsfunktion.

Sind $f_s(q)$ Polynome von q (Vgl. (18)) mit constanten Koeffizienten, so hat die allgemeinste Wirkungsfunktion die Gestalt

$$\mathfrak{S} = [f_0(q) + f_1(q)A_1 + f_2(q)A_2 + f_3(q)B_1 + f_4(q)B_2 + f_5(q)B_3 + C] \sqrt{g} \quad (21)$$

C bedeutet hier eine ganze rationale Funktion von Invarianten (14).

Von dieser Wirkungsfunktion ausgehend, wären nun die Feldgesetze aufzustellen. Dies ist bisher nur für die einfachsten Invarianten durchgeführt worden.

Bacteriology. — “*Studies on the bacteriophagus of d’HERELLE*”.
By J. W. JANZEN and L. K. WOLFF. (Communicated by Prof.
C. EYKMAN).

(Communicated at the meeting of May 27, 1922).

IV. *About the relation between bacteriophagus and resistant bacteria.*

d’HERELLE tells us in his book that, when a weak bacteriophagus is added to a thick emulsion of bacteria, the former will have disappeared from the suspension after some time.

Then he says that the bacteriophagus also seems to penetrate into the bacteria, but that, now that the bacilli could not increase, the bacterium resists the bacteriophagus, which is destroyed in vivo. We have considered it important to study this phenomon carefully once more; for this we have used some typhoidbacteriophagi, one resistant and one not resistant typhoidstrain out of our collection.

We have found that the disappearance of the bacteriophagus as described by d’HERELLE for thick emulsions also takes place in the ordinary thin emulsions, this time not of normal but of resistant bacilli.

We have also found that old non resistant bacilli, which are not being dissolved by the bacteriophagus in consequence of their age, do absorb the latter; in this case however, the bacteriophagus only increases when the bacteria multiply and so get young again.

Some of the series of experiments about this subject are as follows:

Series of experiments I.

Resistant strain = T 20. Non resistant strain = T Wi.

Determination of the number of bacteriophagus germs by counting the number of islands (on agarplate).

Bacteriophagus Wi,

Adding equal portions of bacteriophagus Wi to equally turbid suspension in broth of T 20 and T Wi.

Number of bacteriophagus germs per cm^3 .

| | T 20 | T Wi. |
|-------------|---------------|-------------|
| Directly | (18 milliard) | 18 milliard |
| 1/4 hour | 0.6 " | 0.28 " |
| 3/4 hour | 2.4 " | innumerable |
| 1 1/2 hours | 0.8 " | " |
| 24 hours | 0.02 " | " |

A second experiment with T (Sm) instead of T (Wi) offered an analogous result.

| | T 20 | T Sm. |
|----------------|---------------|-------------|
| Directly | (30 milliard) | 30 milliard |
| after 1/4 hour | 1.7 " | 4 " |
| " 1 hour | 4 " | 100 " |
| " 24 hours | 1.8 " | innumerable |

After a week the number of bacteriophagus germs with the resistant strain was about the same as the number found after 24 hours; with the non resistant strain it had greatly increased.

We have regularly found the slight increase (in comparison with the number after 1/4 hour and after 3/4—1 hour) with the resistant strain; the explanation seems to us as follows: the resistant strain also has some weaker descendants which can be dissolved by the bacteriophagus; hence an increase of the bacteriophagus, which is now being caught by the stronger brothers.

We can easily succeed in destroying the bacteriophagus by culturing three or four times on broth with new bacilli the mixture of bacteriophagus-resistant strains in fresh broth.

| | |
|--|---------------------------------|
| I. 1st culture of bacteriophagus germs | 60 milliard per cM ³ |
| 2nd " " " " | 24 " " " |
| 3rd " " " " | 1/4 " " " |
| 4th " " " " | disappeared? |
| 5th " " " " | disappeared |

| | |
|---|-------------------------------|
| II. 1st culture of bacteriophagus germs | 18 milliard per cm^3 |
| 2nd " " " | 0.02 " " " |
| 3rd " " " | disappeared |

Finally an experiment with old non resistant bacilli.

A. 14 days old bacilli *Sm* in broth.

B. 6 hours old bacilli *Sm* in broth.

| A. | B. |
|------------------------------|--------------|
| Directly (30 milliard) | 30 milliard |
| after $\frac{1}{4}$ hour 4 " | 6 " |
| after $\frac{3}{4}$ " 2 " | 800 " |
| after 2 " 32000 " | Innumerable. |

Our typhoid bacilli that are resistant by nature to the bacteriophagus do not even lose their resistance after being subcultured repeatedly in contradistinction to what D'HERELLE tells us in his book (pag. 67) about the bacilli, who are been made resistant by influence of the bacteriophagus.

V. About big and small islands.

O. BAIL and T. WATANABE have said that, in plating a mixture of bacteriophagus and bacteria cultures on agar plates, the islands are not always equally big, but that sometimes big ones, medium ones and small ones are to be found.

They have tried to cultivate the bacteriophagus of these islands purely; they say that they have succeeded in doing this with the small islands, not with the big ones however.

We too had already been struck by this before BAIL's communication reached us, and we have tried to isolate these bacteriophagi, forming big and small islands, from each other, but we did not succeed. We have stated though, that it could not be possible in our cases, as a bacteriophagus which exclusively formed big islands with regard to one typhoid strain, made nothing but small islands with regard to another typhoid strain, and as to a third, both big and small ones. So we do not believe that BAIL's and WATANABE's explanation is right, but we think the difference in size of the

islands must be attributed to a difference of virulence as to the various strains. Big islands point to a strong effect with regard to the typhoidstrain; small ones to a weaker effect. This has also been proved by a still to be published investigation of Dr. KROPVELD in our laboratory, about staphylococci-bacteriophagi.

Bacteriophagus Wi always gives both big and small islands with regard to T Wi.

Small and big islands are cultured over separately 9 times, small islands always being used for the series of small ones, big islands for the series of big ones in this process.

The last culture of both always gave a mixture of big and small islands again.

Finally we have tried both bacteriophagi Wi big¹⁰ and Wi small¹⁰ as to 4 typhoidstrains.

With both bacteriophagusstrains we got exactly the same result which is only following once.

| | 1. Clearing. | 2. Checking. | 3. Islandformation. |
|-----------|--------------|--------------|-----------------------------|
| Typhoid 9 | ++++ | ++++ | ++++ very big islands. |
| " 17 | +++ | ++++ | ++++ big islands. |
| " 27 | — | ± | ++++ very small islands. |
| " Wi | ++++ | ++++ | ++++ big and small islands. |

Laboratorium of Hygiene.

Amsterdam, May 1922.

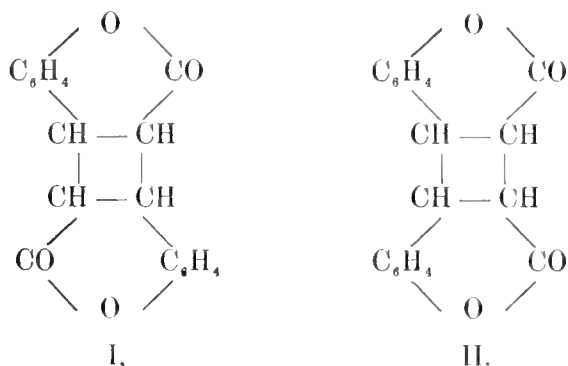
Chemistry. — “*The Biscoumaric Acids*”. By A. W. K. DE JONG.

(Communicated at the meeting of May 27, 1922).

Some time ago ¹⁾ I communicated that the product of illumination of coumarin is not identical with hydrodicoumarin of FITTIG and DYSON, as CLAMICIAN and SILBER had thought, but that it must have another structure, because when treated with alkalis it does not give a mono-basic, but a di-basic acid.

It is natural to suppose that the product of illumination of coumarin is formed from coumarin in the same way as α - and β -truxillic acid are formed from the forms of normal cinnamic acid by the combination with formation of a tetramethylene ring between the doubly bound C-atoms of the two molecules.

As two molecules of normal cinnamic acid can combine in four different ways to a truxillic acid ²⁾ also the combination of two molecules of coumarin will give four different biscoumarins, which will, as the truxillic acids, belong to two series according to the arrangement of the C-atoms with unequal (I) or equal (II) atom-groups next to each other in the tetramethylene ring.



Of both structural formulae two different biscoumarins can exist according to the situation of the coumarinrings on different sides or on the same side of the tetramethylene ring.

¹⁾ These proceedings Vol. XX, 875.

²⁾ These proceedings Vol. XX, 590.

To the product of illumination of coumarin one of these four structural formulae must be assigned.

Also another biscoumarin is known, obtained by KNUT T. STRÖM ¹⁾ by boiling biscoumaric acid, formed by illumination of coumaric acid, with anhydrous acetic acid. This biscoumarin is, as STRÖM already communicated, different from the biscoumarin obtained by illumination of coumarin, nor is it identical with the hydrodicoumarin of FITTIG and DYSON.

The biscoumaric acid of STRÖM is formed from coumaric acid, of which no metastable forms are known till now, in a conformable way as α -truxillic acid of α -normal cinnamic acid, and therefore it is very likely that this biscoumaric acid will have a conformable structure to α -truxillic acid. The properties of this biscoumaric acid known at present are in agreement with this, as will be shown.

The biscoumarin of STRÖM would then possess the structural formula I, the coumarin-rings being situated on different sides of the ring.

To distinguish the different biscoumaric acids I propose to give to these acids similar names as to the truxillic acids, and then the biscoumaric acid of STRÖM must be called α -biscoumaric acid, and its biscoumarin α -biscoumarin. The melting- at the same time decomposition-points of the two substances are the same, viz. 318° (STRÖM stated them to be above 275°); α -biscoumaric acid also changes into its biscoumarin when heated to 250° . The biscoumarin obtained by illumination of coumarin might be different from α -biscoumarin by the position of its coumarin-rings situated, on the same side of the tetramethylene-ring or it might be one of the two other possible biscoumarins indicated by figure II. The first supposition was not very likely, the two biscoumarins showing no change when heated at 210° with the acetic acid anhydride, whilst, when they had only a difference in the situation of the coumarin-rings with respect to the tetramethylene-ring, a change of one into the other was probable. This experiment is, however, not a conclusive proof of a different binding of the coumarin-molecules in the biscoumarins. The best way to decide this is to prepare the acid of the biscoumarin, converting it to the dimethylether, and to try if through heating with the acetic acid anhydride at 210° an anhydride is formed which gives a dimethylether of another biscoumaric acid. If the two coumarin-rings are situated on the same side of the tetramethylene ring, no other biscoumaric acid is formed, whilst

¹⁾ Ber. **37**, 1383.

when they are on different sides, a new biscoumaric acid will be obtained.

The methylation of α -biscoumaric acid by dimethylsulfate gives the dimethylester of the dimethylether crystallized into needles, melting at 133° and sparingly soluble in ether. On boiling with alkalis the dimethylether was obtained melting at 261° — 262° . BERTRAM and KÜRSTEN¹⁾ found the melting point of this substance, obtained by illumination of the methylether of coumaric acid, to be 260 — 262° .

When the dimethylether is heated with the acetic acid anhydride at 210° , the anhydride of the dimethylether of γ -biscoumaric acid was formed, which crystallized in pretty large bright yellow crystals out of the anhydride of acetic acid, melting at 186° — 187° . The dimethylether itself was obtained in fine needles melting at 234° .

When the α -biscoumaric acid is heated with KOH the acid corresponding to β cocaic acid was obtained, which separated in an ether solution by addition of petrolether in rhomb-shaped crystals melting 212° . As it would be strange to give this acid a name connected with coca, I propose to call it ζ -biscoumaric acid. With a similar treatment also the dimethylether of α -biscoumaric acid gave the same acid, which shows that the methylgroups are split off through melting with KOH

These transformations of the α -biscoumaric acid, respectively the dimethylether, are wholly analogous to these of α -truxillic acid.

The dimethylester of the dimethylether of the biscoumaric acid of the product of illumination of coumarin, for which I propose the name of λ -biscoumaric acid, melts at 112° — 113° ; the dimethylether itself at 134° .

By heating the dimethylether with acetic acid anhydride at 210° and after evaporating the solvent in a glycerine bath at about 130° a brown sirup was obtained, which did not crystallize. The acid obtained by boiling the sirup with alkali crystallizes out of an ether-petrolether solution in fine needles melting at 203° . On account of its resemblance in structure with ϵ truxillic acid I propose to call this substance the dimethylether of ϵ biscoumaric acid. This transformation proves that the coumarin-rings of the illumination product are situated on different sides of the tetramethylene ring and as also α -biscoumarin possesses the same situation of the coumarin-rings and the two substances are different, λ -biscoumarin must have the structure of fig. II and by the removing of a carboxylgroup

¹⁾ Journ. f. pr. Ch. (2) 51, 323.

from one side of the tetramethylene ring to another an *o*-dioxo- ϵ -truxillic acid is formed.

By melting with KOH λ -biscoumaric acid is converted into δ -biscoumaric acid, crystallizing in needles melting at 157°.

I hope to make further communications on other possible transformations of the biscoumaric acids, while it will also be tried to obtain them from the truxillic acids, by which the proposed names and the structural formulae will obtain more security.

Laboratory of the Colonial Museum, Haarlem.

Physics. — “*On the Excitation and Ionization Potentials of Neon and Argon*”. By G. HERTZ. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of May 27, 1922)

It is known that rare gases and metallic vapours behave in a very simple way on collision with slow electrons. Then there can be exchange of energy between electrons and atoms only in one way, viz. that in which the transferred energy is used to bring the colliding atom into a higher quantum condition. Hence on collision with the atoms the electrons can transfer only very definite energy quanta to them, which according to BOHR'S theory, are in direct connection with the series-spectrum of the atom. For a great many metallic vapours this transition of energy in quanta has already been investigated and the relation to the optic spectra has been shown. Of the rare gases accurate measurements have only been carried out for helium¹⁾, on the ground of which FRANCK succeeded in making the system of the series-spectra of helium complete, and in showing the connection between the ortho-helium and the parhelium spectrum. Several observations have, indeed, been made for neon and argon²⁾, but the results are inaccurate for the greater part, and partly in conflict with each other. Besides in the great sensitiveness of noble gases to traces of impurities, the excitation and ionization potentials of which lie nearly always below that of the rare gas, the cause of these conflicting results seems to lie chiefly in this that the efficiency of the unelastic collisions in the rare gases is much smaller than in the metallic vapours, so that the methods which lead to good results for the latter, cannot be applied here. In order to attain reliable results, it seemed, therefore, necessary to me, to refine the methods for the investigation of the quantum

1) F. HORTON and A. C. DAVIES, Proc. Roy. Soc. London (A) 95, 408, 1919.
J. FRANCK and P. KNIPPING, Zeitschr. f. Physik, 1, 320, 1920.

K. T. COMPTON, Phil. Mag. 40, 553, 1920.

2) F. HORTON and A. C. DAVIES, Proc. Roy. Soc. London, (A). 97, 1, 1920 and 98, 124, 1920.

G. STEAD and P. S. GOSLING, Phil. Mag. 40, 413, 1920.

H. C. RENTSCHLER, Phys. Rev. 14, 503, 1913.

G. DÉJARDIN, C. R. 172, 1347, 1921.

transition of energy between electrons and atoms, and supplement it by a method which admits of a clear distinction between light emission and ionization also in the case of unelastic collisions of small efficiency.

The methods applied up to now for the study of the quantum emission of energy consist in this that either the radiation or ionization that take place starting from a definite potential, or the phenomenon that the impinging electrons lose energy, is used as a proof of the occurrence of unelastic collisions. In this way a curve is obtained in which the different steps of energy appear as breaks; an accurate measurement of them is often difficult, especially for the higher steps of energy. It seemed, therefore, desirable to me to use as criterion for the quantum transition of energy a characteristic that immediately disappears again when the critical potential is exceeded, and consequently causes the separate steps of energy to stand forth as sharp maxima. Such a characteristic is the occurrence of electrons with the velocity zero. For as soon as an electron possesses exactly the energy required for the excitation of a definite quantum transition, it may lose all its energy at the collision, and be left behind as an electron with the velocity zero. If, however, it possesses a greater energy, it retains the rest after the collision, and remains behind as an electron with a velocity which, though smaller, is yet different from zero. If, therefore, electrons of a definite velocity, are admitted into a space in which they collide with atoms of a noble gas, electrons of the velocity zero will only occur when the energy of the electrons is precisely equal to the work required for the excitation of a quantum transition. When, therefore, the number of electrons which are left behind with the velocity zero, is plotted as function of the accelerating potential, a sharp maximum must be obtained for every potential corresponding with an energy-quantum that can be transferred at a collision of electrons. In consequence of the inevitable distribution of velocity of the electrons it is not possible to determine the number of electrons which have rigorously a velocity zero. Therefore the number of those electrons the velocity of which lies below a definite small value (in our measurements mostly 0.2 Volt) will be plotted as function of the tension.

The measurements according to this principle are carried out in the following way:

The electrons emitted by a short incandescent wire D of tungsten (Fig. 1) enter the field-free space R through the gauze N , after acceleration through an electric field, in which space they collide with the atoms of a rare gas. Part of the electrons passes through

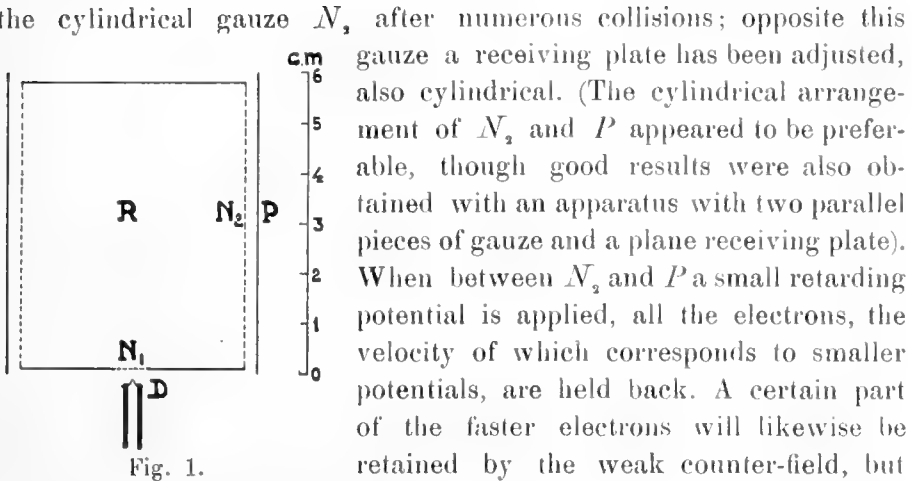


Fig. 1.

the cylindrical gauze N_1 , after numerous collisions; opposite this gauze a receiving plate has been adjusted, also cylindrical. (The cylindrical arrangement of N_2 and P appeared to be preferable, though good results were also obtained with an apparatus with two parallel pieces of gauze and a plane receiving plate). When between N_2 and P a small retarding potential is applied, all the electrons, the velocity of which corresponds to smaller potentials, are held back. A certain part of the faster electrons will likewise be retained by the weak counter-field, but as appears on closer consideration, this part greatly decreases with increasing velocity. The difference between the stream of electrons received on the plate with and without the small counterfield, therefore, gives a measure for the number of electrons having about the velocity zero. In order to be able to measure this difference with great accuracy, an arrangement was chosen which rendered it possible to insert and cut out the field alternately; the part of the potentiometer from which the small counter-potential had been branched off, could be short-circuited by a mercury contact in vacuum. By alternate reading of the deviation with and without counterfield the difference could be accurately read, and an error in consequence of a possible change of the zero-point was out of the question. It is further possible to render oneself independent of a slow change in the emission of electrons of the incandescent wire, by dividing the difference measured by the total deviation. For the efficiency of the method it is of importance that the metal surfaces should have the greatest purity possible, as small impurities can already cause Volta-potential differences of the order of magnitude of the small counter-potential. The copper used had been cauterized with nitric acid immediately before the construction and the sealing in of the apparatus. The whole apparatus was mounted on a pretty large glass foot, as is used for incandescent lamps, so that it could be fused into a glass globe without the metal parts being heated too much. It was heated at 400° in high vacuum for six hours; after this the copper, even though it was a little tarnished before in a few places, presented a perfectly pure metallic surface.

In figures 2 to 4 curves are represented as instances of the results of such measurements, which refer to neon of a pressure of 0,51 m.m., to a neon-helium mixture of 30% helium and a pressure

of 0,56 m.m. and argon of 0,36 m.m. pressure. Especially fig. 3 shows the efficiency of the method. In spite of the comparatively small percentage of helium, the two first excitation tensions of helium, though they lie above the strong excitation tensions of neon,

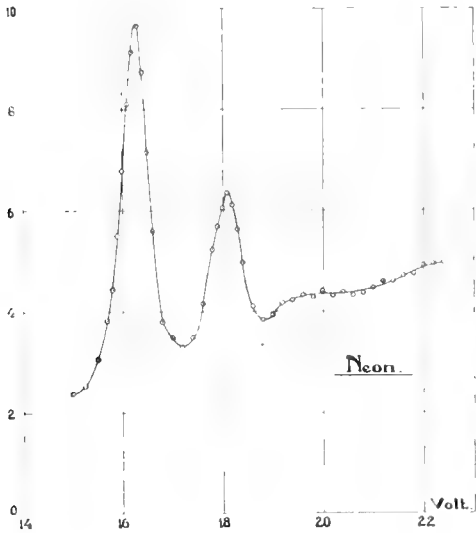


Fig. 2.

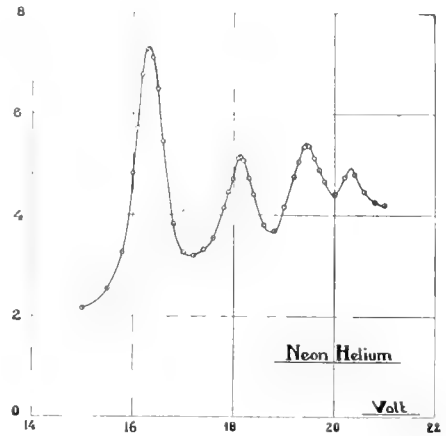


Fig. 3.

stand out as two sharp maxima at a distance of 0,8 Volt. These maxima were used to obtain the absolute value of the excitation tensions of neon, in which the value of 20,45 Volts measured by FRANCK and KNIPPING¹⁾ for the lowest excitation tension of helium, was used as basis. The values thus obtained appeared to be independent to a high degree of the circumstances of the experiment.

This method is entirely unsuitable for the measurement of the ionization-potential. For then the impinging electron or the electron that has been liberated from the atom by the collision can have the velocity zero after an ionizing collision, also when the energy of the colliding electron was greater than the work of ionization. As moreover at first the effect brought about by ionizing collision evidently rapidly increases with increasing tension, the curve shows no maximum here, but only a rise, which is besides influenced by the positive ions, and does not admit an accurate determination of the ionization-potential. For this reason the arrangement usual with a strong counter-field between N_1 and P was used for the measurement of the tension of ionisation for some measurements; most observations were, however, made according to a new method,

¹⁾ J. FRANCK and P. KNIPPING, l.c.

in which a very reliable criterion is applied for the first appearance of the ionization. For this purpose a second, very thin incandescent wire G of the shape represented in Fig. 5 was placed in the field-

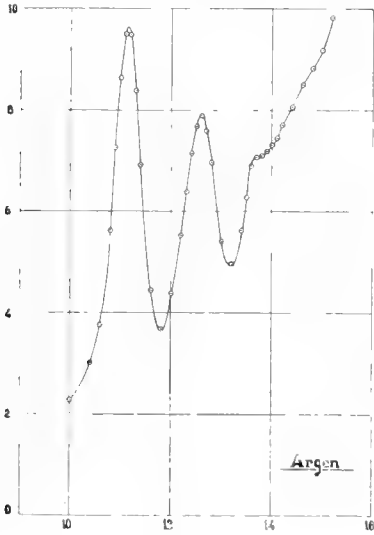


Fig. 4.

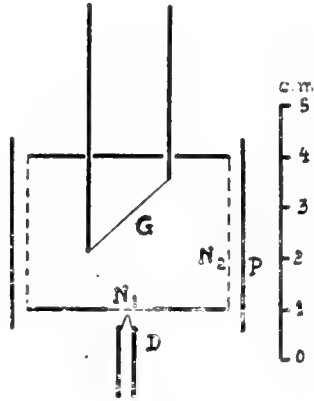


Fig. 5.

free space R ; the positive end of this wire (on the left side of the figure) was connected with the walls of R , so that the field round the wire, which moreover remains restricted to its immediate neighbourhood on account of the slight thickness of the wire, can by no means accelerate the electrons coming from D . This incandescent wire was heated to such a temperature that the stream of electrons flowing from the wire to the metal wall, is limited by the space charge. So long as the energy of the electrons coming from D is not sufficient for the formation of positive ions, they have no influence at all on the amount of the stream of electrons issuing from G . Nor could a photo-electric effect, if it took place, even apart from the fact that it is so small, have any influence on the amount of this stream of electrons, limited by the space charge. As soon, however, as positive ions are formed, and some of them get into the neighbourhood of G , the space charge is partly annihilated, and the stream starting from G suddenly rises. Figures 6 and 7 show the results of these measurements in neon and argon. It is seen that not even the slightest discontinuity can be perceived in the curve when the lower excitation tensions are passed, while at the tension of ionisation the stream begins to rise rapidly. To obtain the absolute value of the ionization potential, the maximum corresponding to the first excitation potential was determined at the same time by the aid

of N_e and P according to the method discussed above, which is likewise expressed in the figures. In this it should be taken into

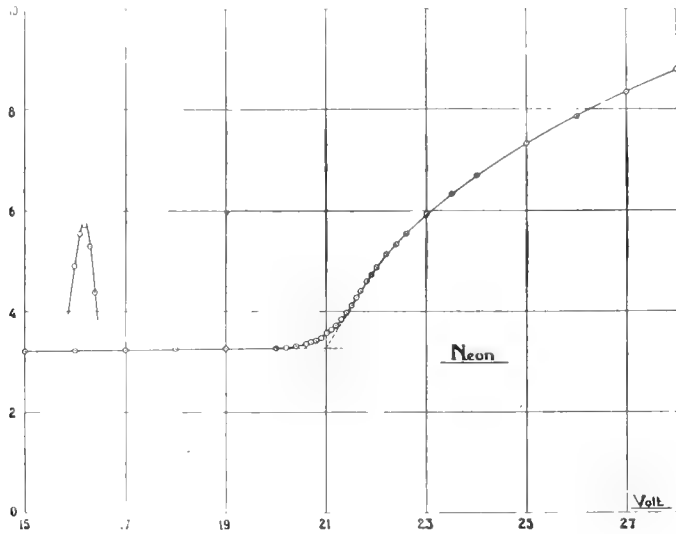


Fig. 6.

account that this maximum slightly differs with respect to the tension at which unelastic collisions take place, viz. the amount equal to the small counter-potential (here 0,2 Volt). It may also be mentioned that the measured stream in these experiments was about

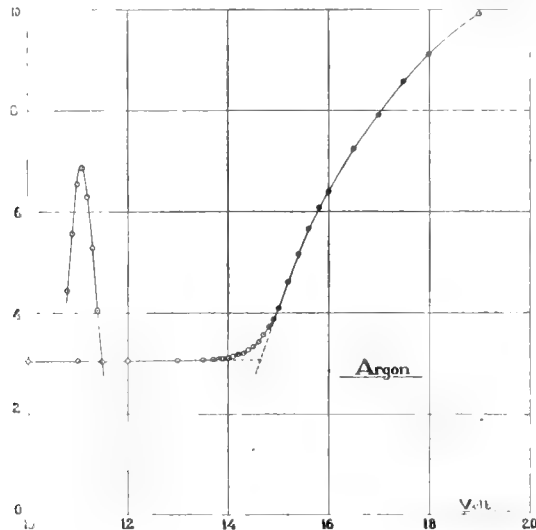


Fig. 7.

thirty times the flow of electrons issuing from D , so that in this way an accurate measurement of the ionization potential is possible, even with an ordinary millivoltmeter.

Results. Starting from the value of 20,45 Volts for the lowest excitation potential of helium, two rather pronounced excitation potentials were found for neon at 17,35 and 19,15 Volts, 22,2 Volts was found for the ionization-potential of neon; for argon two excitation potentials were found at 12,25 and 13,7 Volts, a less distinct one at 14,7 Volts; the ionization-potential at 16,0 Volts.

With the very complicated structure of the optical spectrum of neon the occurrence of discrete fairly pronounced excitation potentials seems surprising at first sight. If, however, the serial scheme of neon drawn up by PASCHEN¹⁾ (fig. 8) is plotted in a scheme in the way given by BOHR, it is directly seen that the values found are in very good harmony with the optical measurement. The term

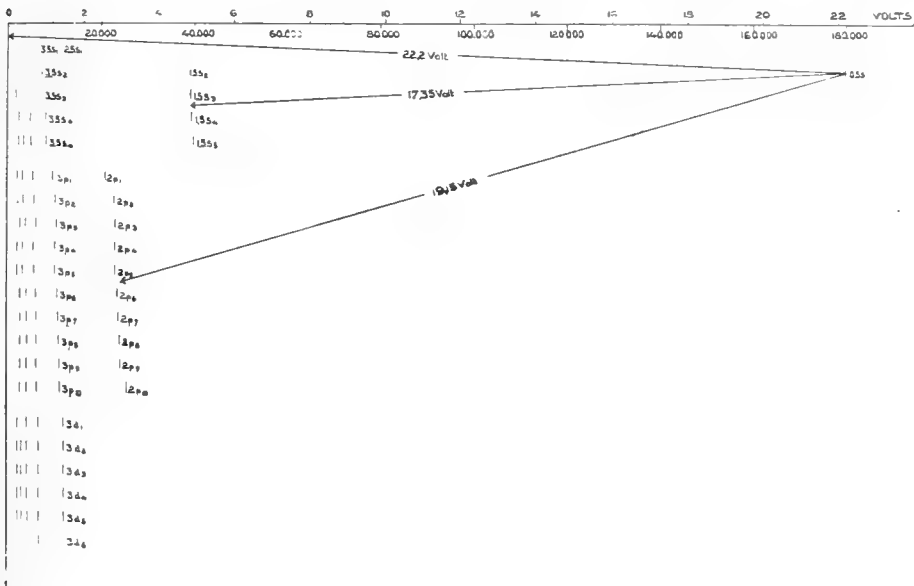


Fig. 8.

corresponding with the normal state and denoted by me as 0,5s has been added in the scheme, the value of this term has been calculated from the ionization-potential. This term 0,5s is first of all followed by a group of four terms of the type of 1,5s; these lie close together within a region which, expressed in Volts, is smaller than 0,2 Volt., and can, therefore, not be separated in measurements with colliding electrons. Then follows a group of 2p terms, the greater part of which lies again within 0,1 Volt. After this come, about 1 Volt higher, the 3d terms. The other terms succeed each other at distances of at most some hundredths of Volts,

¹⁾ F. PASCHEN, Ann. d. Phys. 60, 405, 1919.

so that the methods of the collisions of electrons is not sufficient to separate them, only a "continuous spectrum" can be observed. When the curve given in fig. 3 is compared with this, the serial system is clearly found back in it. The first maximum corresponds to the group of the quantum transitions $0.5s-1,5s$, the second to the group $0.5s-2p$, and then at a distance of 1 Volt follows the spectrum of the transitions to higher quantum conditions, which seems continuous on account of the small dissolving power. Also quantitative the agreement is good, as is seen in fig. 8, where the quantum transitions observed with collisions of electrons have been indicated by arrows, of which the projection on the axis of abscissae is equal to the observed value of the potentials of excitation resp. ionization. It is, therefore, seen that the serial scheme of neon has become complete by the addition of the term $0.5s = 179800 \pm 1000$. There is no room in this serial system for a resonance-potential of 11.8 Volts and ionization-potentials at 16.7 and 20 Volts, which values were derived by HORTON and DAVIES ¹⁾ from their experiments, nor was there any indication at all in my measurements of the occurrence of resonance or ionisation at these potentials. On the other hand the experiments of the same investigators on excitation of light in neon through collision of electrons ²⁾ are in good agreement with the conclusions which may be derived from the completed scheme. As can at once be read from the figure, the lines of the principal series must first appear alone starting from 19.2 Volts, then from about 20.2 Volts the lines of the secondary series must gradually begin to make their appearance, while the whole spectrum only can be emitted above the ionization-potential. HORTON and DAVIES actually found that at 20 Volts only the lines of the principal series were emitted, the whole spectrum not appearing before 22.8 Volts.

It would be of importance to ascertain whether there may perhaps be terms for neon that correspond to metastable states, as FRANCK has found them for helium and mercury ³⁾. To find this out it would, however, be necessary really to separate the different terms, and for this the dissolving power of the method of the collisions of the electrons is not yet sufficient. Measurements with the usual arrangement for showing photo-electric radiation proved, as was to be expected, the occurrence of photo-electrically active radiation at both the excitation potentials observed.

As was already stated above, in *argon* there likewise appear two

1) F. HORTON and A. C. DAVIES, l.c.

2) F. HORTON and A. C. DAVIES, Phil. Mag. **41**, 921, 1921.

3) J. FRANCK, Phys. Zeitschr. **22**, 388, 1921.

excitation potentials (at 12.25 and 13.7 Volts), and a less distinct one at 14.7 Volts, which is followed by a series of energy steps which has not yet been dissolved. Here too the apparently sharp excitation potentials will no doubt correspond with undissolved groups of terms lying close together, on account of the complication of the argon spectrum. The argon spectrum not yet having been split up into series, a comparison is not yet possible. When a similar structure is assumed for the spectrum of argon as for neon, then starting from the measured values for excitation and ionization potentials, the following mean values for the first groups of terms are to be expected:

$$\begin{aligned} 0.5 s &= 130000 \pm 1000 \\ 1.5 s &\sim 30400 \\ 2 p &\sim 18600 \\ \text{higher terms} &< 10500 \end{aligned}$$

The serial terms calculated by NISSEN¹⁾ do not fit in with this scheme. Also the fact that according to NISSEN lines of the red and the blue argon spectra are considered as members of the same series, though the condition for the excitation of the two spectra are different, pleads in my opinion against the validity of the terms calculated by him.

For the rest more complications may possibly be expected for argon than for neon. The fact found by PASCHEN²⁾ that for part of the neon series the limits are shifted by a constant amount in comparison with the other series, was explained by GROTRIAN³⁾ by the aid of the L-doublet of neon. He has also already pointed out that it must be expected for argon that the multiple M-limits will manifest themselves in an analogous way.

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Gloeilampenfabrieken".*

(Philips Incandescent Lamp Works).

Eindhoven.

¹⁾ K. A. NISSEN, Phys. Zeitschr. **21**, 25, 1920.

²⁾ F. PASCHEN, Ann. d. Phys. **63**, 201, 1920.

³⁾ W. GROTRIAN, Zeitschr. f. Phys. **8**, 116, 1921.

Microbiology. "On the Occurrence of Sulphate-reduction in the deeper layers of the Earth". By C. A. H. VON WOLZOGEN KÜHR. (Communicated by Prof. G. VAN ITERSON JR).

(Communicated at the meeting of April 29, 1922).

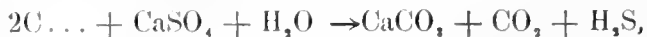
§ 1. *Introduction.*

The disappearance of organic matter at greater depths in the soil has since long occupied the minds of investigators. The difficulties associated with their inquiries regard especially that of obtaining sterile samples from such depths, which is essential to microbiological inquiry.

The process of oxidation, which causes organic matter to disappear, can be effected by free as well as by combined oxygen. When the air is shut off, as is the case in the lower strata, oxidation is of course brought about by combined oxygen.

Now the question is how this process can take place microbiologically.

The term sulphate-reduction designates the process by which, with the exclusion of air, organic matter in the soil is oxidized under the influence of combined sulphate-oxygen. This anaerobic process is effected by *Microspira desulfuricans*, discovered in 1895 by BEIJERINCK¹⁾. It being an exothermic process energy is set free through this oxidation, which is utilized physiologically by the sulphate reducing spirilla. The rough equation for sulphate-reduction gives the following formula:



in which C... is the symbol for the source of carbon.

Microspira desulfuricans occurs in the mud of ditches and the ooze of the Dutch "Wadden". The grey, bluish-black to black colour of the soils in which sulphate-reduction takes place, must be ascribed to ferric sulphid, in which form the liberated hydrogen sulphid is combined by iron-compounds present in the soil.

The occurrence of the sulphate-reducing microbe at the greater depths in the terrestrial soil has been less frequently observed and,

¹⁾ Ueber *Spirillum desulfuricans* als Ursache von Sulfatreduktion. *Verzamelde Geschriften*. 3de deel, pg. 102.

to my knowledge, statements about it are few and far between. JENTZSCH¹⁾ e.g. records that in the deeper ooze-layers of the ocean of about 40 m. and more, reduction-processes occur, in which hydrogen sulphid and ferric sulphid are formed, which are ascribed by him to decomposition of proteins. It is more likely, however, that here also we have to do with sulphate-reduction, since it has been proved that this is of frequent occurrence under the circumstances alluded to.

Another statement is given by EUG. DUBOIS²⁾ who observed the transformation of sulphate into ferric sulphid in the lower alluvial clay-layers underneath the Dutch Dunes.

An opportunity to ascertain the occurrence of sulphate reduction in deeper layers was offered, when in the autumn of 1921 a number of new wells were dug along the Sprenkelkanaal on the source of supply of the Amsterdam Dune Waterworks.

§ 2. *How the samples of sand, clay and peat were obtained from the well-shafts.*

In connection with the bacteriological sampling it will be well to set forth, in principle, the way in which the new wells were sunk.

A wide iron tube is driven vertically into a dug, shallow cavity. The sand is excavated from a greater depth than is at first reached by the tube, which can consequently sink gradually deeper. By means of a screw-thread one length of tube is screwed on to the other, so that a system of tubes is procured of the length necessary to reach a certain depth.

The masses of sand and the occasional lumps of clay and peat are removed from the tubes with a so-called "puls", consisting of a hollow iron cylinder of smaller diameter than the tube's. At the lower end it is sharp-edged to facilitate the sinking, while the bottom is provided with a valve, opening to the inside. By means of two iron bars that are fastened to the edge of the open top-part of the cylinder and are suspended on the same point of support, it is possible to connect the apparatus to a pulley-block. When moving the "puls" forcibly up and down in the wet mass of sand present in the shaft, it is ultimately filled with a pap of sand. The filled "puls" is then hoisted up and emptied by overturning it. This process of removing the sand from the well-shaft is briefly called "pulsen".

¹⁾ Zeitschrift d. Geol. Ges. 1902. 54, p. 144. Cf. RAMANN, Bodenkunde, p. 180.

²⁾ Het Leidsche Duinwater. Eene hydrologische studie. 1912, p. 19 en 20.

§ 3. *The examination of the sand- and clay-samples for sulphate-reduction.*

From a chemico-biological point of view it is interesting to ascertain the origin of the ferric sulphid, which gives a dull-grey, greyish blue to bluish-black colour to the soil-samples. The obvious hypothesis that the ferric sulphid was formed by sulphate-reduction, was in every respect substantiated by the examination of the many sand-, and clay-samples procured by means of the "puls". Thus the sulphate reduction in the deeper layers of the earth underneath the dunes appeared to be a bacteriological process of common occurrence.

The demonstration of sulphate reducing spirilla was performed after the accumulation-method of BELJERINCK, the culture-medium ¹⁾ used being:

| | |
|-----------------------------------|------------------|
| Tapwater | 100 |
| Na-lactate | 0.5 |
| Asparagin | 0.1 |
| MgSO ₄ . 7 aq. | 0.05 (or gypsum) |
| FeSO ₄ . 7 aq. | 0.001 |

with which sterile stoppered bottles of ± 150 cc. capacity were filled after infection with a quantity of the sand-, or clay-samples under examination. They were filled up to the neck, then cautiously stoppered and placed under 25° C.

BELJERINCK ²⁾ showed that in this anaerobic procedure *Microspira desulfuricans* is exclusively the causative agent of the sulphate-reduction manifesting itself, as appears from the formation of hydrogen sulphid and the black ferric sulphid.

My culture bottles showed in every respect the same progress of the reduction process, so that hereby the examined sand-, and clay-samples gave evidence of the presence of *Microspira desulfuricans*.

The material used for infection of the medium was drawn from the inner portion of the sand-mass in the "puls" by means of a sterile spatula, and deposited in sterile wide-mouthed stoppered bottles. Directly when the samples were received at the laboratory they were subjected to investigation.

Sterile sampling could be effected to perfection only in clay-, and peat-samples. This was performed after BELJERINCK's ³⁾ method. The sample was split in two. From the fracture laid bare, the required

¹⁾ A. VAN DELDEN. Beitrage z. Kenntn. d. Sulfaatreduktion durch Bakt. Centralbl. f. Bakt. 2e Abt. 1903. Bd. XI, p. 83.

²⁾ Verzamelde Geschriften. (Collected Papers) Vol. 4, p. 53.

³⁾ Verzamelde Geschriften. (Collected Papers) Vol. 2, p. 354. Note 2.

inoculation material was taken by means of a sterile spatula. The lumps of clay and peat suited our purpose well, since in the splitting the fracture was not contaminated by crumbling particles of the edges, which was owing to the solid structure of the samples resulting from their humidity.

The time in which the formation of hydrogen sulphid in the culture-bottles commenced was very different for the same inoculation-substance and especially for the sulphate reduction it largely depends on the number of viable germs present at the outset of the experiment.

The clay-, and the peat-samples dredged up with the "puls", were derived from the clay-, and the peat-banks underlying the dunes. They were all compact masses, in which the original stratified structure, arising from sedimentation, had been preserved. These clay-, and peat-layers being all but impermeable to water, their inside represents the original bacteriological condition of the stratum, from which the sample has been taken.

The clay- and peat-lumps were on the outside wet and on the inside, judging superficially at least, moderately humid. The water-content of the clay amounted to about 26%; in the clay-samples which contained peat in the stratified structure, the content of moisture was considerably higher, viz. about 50%. The peat-samples exhibited the largest amount of water, viz. rather more than 77%.

The clay- and the peat-lumps varied from very large ones to those of the size of a fist and appeared to meet the bacteriological requirements in every respect.

§ 4. *Summary of results and observations on the inquiry about sulphate-reduction.*

The number of soil-samples of the 9 wells which were examined for sulphate-reduction, have been summarized in the subjoined table.

The quantum of infection-material used for every sulphatereduction-test amounted to from 5 to 10 grs. of the soil-sample. After an interval of from 3 to 20 days sulphate-reduction revealed itself at 25° C., which period rose to 5 weeks in the case of the peat-sample B 31.

In every well, even the deepest of 34.50 m. below A.P., we chiefly found sand over the whole depth, in which irregularly spread lens-shaped clay-, and peat-layers occurred alternately.

With a few exceptions all the sand- and clay-samples indicated in the subjoined table, yielded on examination for sulphate-reduction a conclusive positive result. Consequently the dull-grey or grey colour

of the sand-samples and the mostly blue to bluish-black colour of the clay-samples points to prevailing sulphate-reduction. This com-

| B 22 | B 24 | B 25 | B 26 | B 27 | B 28 | B 29 | B 30 | B 31 |
|---------|----------|----------|---------|-----------------|---------|------------------------|---------|---------|
| 21.6 M. | 35.34 M. | 35.30 M. | 6.50 M. | 8.00 M. | | 6.50 to 10.50 M. | 9.50 M. | 8.00 M. |
| | | | 15.10 » | <i>13.25*</i> » | 6.00 M. | 14.00 to | 12.50 » | 14.00 » |
| | | | 17.50 » | | 6.50 » | 16.25 » | 18.50 » | 25.30 » |
| | | | 28.50 » | | | 20.50* » | 32.50 » | (peat) |
| | | | 32.50 » | | 29.00 » | 23.10 » | 34.50 » | |
| | | | | | 34.50 » | | | |

B 22, B 24, etc. = wells.
 The values express in metres the depths below A.P. (= Amsterdam level) from which the soil samples have been drawn.
 The figures in italics refer to clay-samples which enclose organic particles or peat-layers.
 The figures in ordinary type are sand-samples.
 (*) = no sulphate reduction in culture bottle.

mences at about 10 m. below the surface (7.5 m. —A.P.)¹⁾ to ± 37 m. (34.50 m.—A.P.) the largest depth examined here.

The conditions under which sulphate-reduction appears are:

1°. Absence of oxygen²⁾.

2°. The occurrence of organic compounds.

3°. The presence of sulphate and the required mineral compounds.

The first condition, the absence of oxygen, is satisfied in consequence of the considerable depth below the level of the ground.

The second condition: the occurrence of organic compounds, is fulfilled already to the eye by the peat-sample and also by the clay-sample with enclosed peat-layers. That the sand-, and clay-samples, which do not enclose immediately distinguishable organic particles, also contain organic matter, can be demonstrated chemically, by the potassiumpermanganate method. This is conducted as follows: The soil-sample is boiled with diluted sulphuric acid and filtered. The filtrate is cooled down under the tap; now potassiumpermanganate (0.01 norm.) is instilled. The first drops are directly decolorized, which is owing to the oxidation of ferro- and mangano-compounds,

¹⁾ The grounds of the wells at the Sprengelkanaal is lying at 2.5 M. above A.P.

²⁾ Traces of oxygen are left out of consideration here.

Then a moment follows in which the colour of the added potassium-permanganate disappears only slowly: this is the oxidation of the organic matter, extracted by the diluted sulphuric acid, for in a drop of this extract, placed on a piece of filterpaper soaked with potassium ferrocyanid no ferro can be demonstrated any more.

The sand-samples are most often not so rich in organic compounds as the clay-samples, which often contain peat. Presumably this generates a stronger sulphate-reduction than is possible in the sand-samples, and this is probably the reason why clay can be darker in colour than sand.

VAN DELDEN ¹⁾ has shown that for sulphate-reduction organic bodies are required which are easily oxidizable. This justifies the assumption that in the organic substances, demonstrated by us, there are some bodies difficult of oxidation and others again which are easily oxidizable, which is proved indirectly by the sulphate-reduction that manifests itself in the sand-, clay-, and peat-samples.

Also the 3rd condition, the presence of the required mineral compounds, was satisfied. In our examination for sulphate only small amounts could be demonstrated, which is explained by the disappearance of sulphate through sulphate-reduction.

One of the mineral combinations is that of the insoluble, black-coloured ferric sulphid, formed by the iron and the liberated hydrogen sulphid, as pointed out already in § 3.

From the foregoing we may deduce that the conditions of anaerobic life which we found in the deeper layers of the soil, fairly agree with the prevailing sulphate-reduction.

§ 5. *The content of „aerobic” and „anaerobic” germs of the deeper layers of the soil.*

Besides the demonstration of sulphate-reducing spirilla in the soil-samples, another question arises, viz. whether they contain other germs and whether these belong to the aerobes or the anaerobes. We examined the samples:

- B 28 29.00 M — A.P. (clay with peat)
 B 29 6.50 — 10.50 M — A.P. (clay).
 B 31 25.30 M — A.P. (peat).

The number of germs was ascertained in the way described in § 3. With a sterilized spatula inoculation-material was taken from the soil-samples, it was then shaken up in sterile tapwater and

¹⁾ Centralbl. f. Bakt. Bd. XI, 2te Abt. 1903, p. 83.

subsequently weighed. This material was used for making counting-tests by sowing the micro-organisms on nutrient gelatin. The counting of the microbe-colonies for the aerobic plate-cultures took place after 48 and 72 hours, after which there was hardly any increase of the colonies worth mentioning.

The anaerobic culture plates for the counting-tests were made after WRIGHT and BURRI's¹⁾ culture method, modified by me. As this strictly anaerobic method of cultivation yields very good results, it will not be amiss to state our procedure.

In a glass box closed tightly by a glass stopper with a ground rim a smaller petri-dish is placed containing a solidified culture-medium on which the anaerobes are sown in streaks. The circular open space left round the dish is first stopped up with non-absorbent cotton-wool on which a layer of absorbent cotton-wool is laid. The latter is soaked with 20 % potassium hydrate and finally with an equal volume of 20 % pyrogallic acid.

Throughout this procedure the petri-dish remains covered. After the cotton-wool has been soaked with pyrogallic acid the dishcover is removed, while the glassbox is closed by its cover-glass of which the glass-rim is smeared with vaselin. The rim of the glass-box may also be shut off with paraffin after the lid has been adjusted. In order to facilitate the opening of the glass-boxes, the wall is provided with a little hole which is shut off with paraffin and is opened again before taking off the lid of the box, in

| Soil-sample. | Aerobes. | | Anaerobes. | |
|--------------------------------------|-----------------------------------|---------------|-----------------------------------|----------------|
| | number of germs per c.c. of soil. | | number of germs per c.c. of soil. | |
| | After 48 hrs. | After 72 hrs. | After 4 days. | After 12 days. |
| B 28 29.00 M. — A.P. clay + peat. | 15400 | 20000 | 818 | 409000 |
| B 29 6.50—10.50 M. — A.P. clay. | 20 | 130 | — | 400 |
| B 31 25.30 M. — A.P. peat. | — | 7000 | 103600 | 160000 |

¹⁾ J. H. WRIGHT. A method for cultivation of anaerobic bacteria. Centralbl. f. Bakt. 1te Abt. 29, 1901, pg. 61. R. BURRI. 2te Abt. 1902. 8, pg. 533.

order to admit the air. Now the cover of the petri dish is easily removed.

The number of anaerobes was counted in the same way as that of the aerobes in the same sample.

Because we had determined the specific weight of the soil-samples, we could establish the number of germs per cc.

Our results we have tabulated on page 7.

The time in which the anaerobes yielded a constant number of colonies was considerably longer than that of the aerobes.

It strikes us that the anaerobic test yields a total of germs which is much greater than that of the aerobic one, while the amount of germs in B 28 and B 31 is much higher than that of B 29. The last-named fact is perhaps due to the higher content of organic matter in the first two soil-samples.

For the sake of comparison we may add that in raw water from the dunes the number of bacteria per c.c. varies in round numbers from 400 to 1800.

§ 6. *It appears that microbes derived from aerobic and anaerobic cultivation belong for the greater part to the facultative anaerobes.*

The number of species of bacteria obtained in the preceding paragraph by the method described, appeared to be only small when we examined their qualities. Generally the anaerobes and the aerobes ¹⁾ were not identical. The following table shows the number of species of microbes we found:

| Soil-sample. | Aerobes. | Anaerobes. |
|----------------------------|-----------|------------|
| B 28 29.00 M. — A.P. | 2 species | 4 species |
| B 29 6.50 — 10.50 M — A.P. | 2 „ | 1 „ |
| B 31 25.30 M. — A.P. | 1 „ | 4 „ |

As to their properties aerobes revealed some resemblance in acidformation from glucose, Berlin-blue formation from ferri-ferri-cyanid, the formation of hydrogen-sulphid from broth (lead-carbonate test), the splitting of aesculin, the formation of katalase, and most often in the inability to ferment glucose, to form lipase and diastase. Spores were not formed.

¹⁾ Probably B 29 anaerobe and one of the species B 29 aerobe were identic.

A difference in the properties of the two microbe-groups appeared from the following reactions: Anaerobes form nitrite from nitrate in a marked degree, indican is split extensively in most cases (oxidation of indoxyl to indigo-blue), a moderate amount of invertase is formed, a large amount of slime (wall-matter) is formed from saccharose. Aerobes lack these qualities. They liquefy gelatin, whereas the anaerobes do not.

My investigation into the properties of the microbes did not put me in a position to classify them.

When examining microbes derived from aerobic cultivation for their anaerobic behaviour, it appeared that only B 31 grew very well without air, those of B 28 and B 29, however, very badly. The occurrence of these aerobes seems to show that presumably very small quantities of air are to be found at larger depths in the soil, and that they are carried along with the rainwater that penetrates at a very slow rate into the deeper layers of the earth. If the layer, as is the case here with clay, is only sparingly permeable to water, the dissolved oxygen is allowed to diffuse to the places where it is to be consumed.

The microbes obtained from anaerobic cultivation developed enormously when living in air. This appeared conclusively when the anaerobic culture-boxes after being opened had been standing for some time exposed to the air. Then the microbe colonies grew larger and larger in a very short time. These bacteria grew very well as aerobes, also on nutrient agar-slants. Tested in this way the majority of the isolated bacteria appeared to belong to the *facultative anaerobes*, which is consistent with the occurrence of these microbes at greater depths.

§ 7. *Research for some other specific species of microbes.*

We endeavoured to ascertain the occurrence of obligate-aerobic nitrifying bacteria and of *Azotobacter chroococcum*, however, with negative result, as could be expected.

Nor could denitrifying microbes be demonstrated; no more could we detect anaerobic butyric bacteria and anaerobic bacteria which break down cellulose.

§ 8. *VAN DER SLEEN'S Manganese-Theory for the oxidation of organic matter at greater depths in the soil.*

The problem of oxidation of the organic matter in the deeper layers of the earth has been discussed by W. G. N. VAN DER SLEEN

in his publication: „Bijdrage tot de kennis der chemische samenstelling van het duinwater in verband met de geo-mineralogische gesteldheid van den bodem.” The writer says (p. 50) that at such a great depth bacterial influence on the oxidation of organic matter seems to be out of the question and he suspects manganese salts to act as oxygen-carriers. Further on (pg. 62) the writer says: „. . . . I do not think that *Microspira desulfuricans* occurs at such a depth as has to be assumed when ascribing sulphate-reduction only to this micro-organisme”.

On pag. 51 the author records some experiments which go to show that manganese can transmit oxygen from the sulphates to an organic compound such as hydrochinon. To conclude from this that the oxidation of organic matter at the lower depths in the soil could occur in the same way, seems to me hardly admissible unless experimental evidence be brought forward that biological oxidation is out of the question. Such evidence has not been produced as yet. It may be deemed surprising that the author, who, as appears from the passage in his publication that we quoted just now, had taken cognizance of the bacteriological sulphate reduction has omitted to inquire into it. This is the more surprising since on the ground of its anaerobic behaviour *Microspira desulfuricans* is adapted to living at greater depths in the soil.

The evidence produced by our investigation set forth in the preceding paragraphs, by which it has been established that sulphate-reduction is of common occurrence at the greater depths underneath the dunes, warrant the conclusion that oxidation of organic matter can be effected by *Microspira desulfuricans*, without the additional influence of manganese compounds.

§ 9. *The transformation of sulphate in the clay-containing soil of the dunes and sulphate-reduction by *Microspira desulfuricans*.*

The “Koninklijke Academie van Wetenschappen te Amsterdam”¹⁾ has brought forth a report on the question to what the presence of so called Artesian water in the dune-soil is due, in a preliminary advice from G. A. F. MOLENGRAAFF and EUG. DUBOIS. In an enumeration of the chemical properties of dune-water the report contains the following statement:

¹⁾ Verslag v. d. gewone vergaderingen der Wis- en Natuurk. Afd. Vol. XXX, p. 212.

“From the surface downwards in and underneath the dune-masses the sulphuric acid content diminishes proportionally to the total thickness of the clay-layers occurring in them, i. e. in proportion to the increase of the volume of clay-soil, through which the water has percolated downwards.

This phenomenon is the result of the power of clay-soil to convert sulphuric acid and then retain it”.

In the study by Eug. Dubois¹⁾ already quoted above, a detailed exposition is given of the transformation of sulphuric acid in the clay-layers, which consists in a reduction-process in the presence of organic matters, with formation of ferric sulphid.

It is evident from the foregoing that sulphate-reduction, which occurs not only in the deeper clay-layers, but also in the sand-soil, is brought about by Microspira desulfuricans. The life of this microbe, which is adapted to anaerobic conditions, accounts for the common occurrence of sulphate-reduction in the deeper layers of the earth and especially in the clay-soil, which generally has a higher content of organic matter.

So long as the conditions of this typically microbiological process are fulfilled, transformation of sulphate into ferric sulphid will hereby be generated, to which is to be ascribed the partial or total absence of sulphuric-acid salts in deep-dune water.

Heemstede, February 24 1922.

¹⁾ „Het Leidsche Duinwater”. Een hydrologische studie, 1912, p. 20.

Chemistry. — “*The Influence of a Catalyst on the Thermodynamic Quantities Regulating the Velocity of a Reaction.*” By E. VAN THIEL. (Communicated by Prof. J. BÖESEKEN.)

(Communicated at the meeting of May 27, 1922).

According to GULDBERG and WAAGE's hypothesis the velocity of reaction in a homogeneous system of constant temperature is equal to the product of the active masses of the converted substances multiplied by the velocity constant. This constant is, of course, variable with the temperature, and dependent on the nature of the reacting molecules. The differential equations of G. and W. only indicate the number of molecules decomposed in the time unit; they do not indicate precisely how the reaction(s) takes place; hence they do not show either how the reaction constant depends on the nature of the substances and on the temperature.

Disregarding NERNST's formulation, in which the velocity of reaction is put $= \frac{\text{chemical force}}{\text{chem. resistance}}$, a formula that proved untenable,

GOLDSCHMIDT's attempt¹⁾ to give an explanation of the nature of the reaction constant may be called the first. Starting-point for these and following theories were especially two considerations referring to bi-molecular gas reactions:

1. the reaction constant (velocity for concentration = 1) is doubled about per 10° of increase of temperature, so long as the observations are not too far from room temperature. The number of collisions of the molecules is proportional to the translatory velocity, hence proportional to \sqrt{T} . The increase of this kinetic energy can, therefore, contribute to a maximum of 2% to the increase of the velocity of the reaction found. Hence a deeper insight into the nature of the reaction than is given by G. and W.'s theory is necessary.

2. if all the molecules of the decomposed gas were in the same state, every collision would be followed by a reaction. Every reaction would then take place with the same explosive velocity. This not being the case, all molecules are not equally reactive. A fraction of them is in a more favourable condition. It is, therefore, possible that the velocity of reaction is proportional to the number of these

¹⁾ Diss. Breslau, 1907. Cf. also TODD and OWEN, Phil. Mag. 37, 224.

favoured molecules. Whether it is necessary for the reaction that *two* active molecules collide, or whether it is sufficient when *one* of them is active, must for the present remain an open question.

GOLDSCHMIDT assumed that the velocity of reaction is about proportional to the number of molecules the translatory velocity of which exceeds a definite minimum value. Only *these* molecules, the number of which is given by MAXWELL'S law of partition, would be active. This restriction to the velocity of translation, is however, entirely unfounded; it is on the other hand more probable that also the intermolecular and interatomic energies play a part in the reaction, it is, therefore, more plausible to assume a threshold value also for these energies.

KRÜGER'S theory is of a more exact character; it has, however, only been elaborated for the simplest cases, as e. g. the dissociation $I_2 \rightleftharpoons 2I$, in which the reacting substances are already in atomic (active) condition. TRAUTZ gave a more general theory of velocities of reaction. Starting from VAN 'T HOFF'S reaction-isochore:

$$\frac{d \ln K}{dT} = -\frac{Q}{RT^2}, \text{ he substituted for } K = \frac{k_1}{k_2} \text{ and for}$$

$$Q = Q_0 + \sum r_1 \int_0^T c'_v dT - \sum r_2 \int_0^T c''_v dT.$$

He further assumed that k_1 resp. k_2 depends only on the properties of the initial resp. resulting substances, and therefore split the reaction isochore into two parts, each referring to this. For this it must also be possible to split Q_0 rationally, for which purpose T. introduces the conception *intermediate substances* (which have an exceedingly short period of existence). In the case of the splitting up of $2HI \rightleftharpoons H_2 + I_2$ these intermediate substances might be H- and I-atoms. For the decomposition of HI into H- and I-atoms a dissociation energy is again required, in the formation of H_2 and I_2 from these atoms a heat Q_2 is liberated. It is clear that $Q_0 = Q_1 - Q_2$. Now all the obstacles to the splitting up of the reaction isochore were removed, and the following equation resulted:

$$\frac{d \ln k_1}{dT} = -\frac{Q_1}{RT^2} - \sum r_1 \int_0^T c'_v dT / RT^2.$$

By integration and further elaboration TRAUTZ obtained a formula which in approximation could be reduced to a considerably simpler form, and from which some important conclusions may be drawn:

$$\log k = (25 \text{ to } 35) - \frac{Q_1}{4,571 T} - \sum v \cdot 1,5 \log T - \sum v \cdot 1,1$$

while the following form may be derived for the temperature coefficient of the reaction constant:

$$\frac{k_{T_2}}{k_{T_1}} = e^{\frac{Q_1}{R} \cdot \frac{T_2 - T_1}{T_2 T_1} - \frac{\sum v}{R} \int_0^{T_2} \frac{dT}{T^2} \int_0^{T_2} c_v dT + \frac{\sum v}{R} \int_0^{T_1} \frac{dT}{T^2} \int_0^{T_1} c_v dT}$$

From the first of the two equations may be read that in bi-molecular reactions the velocity is *greater*, as the Q_1 is *smaller*, while it follows from the second equation that the temperature coefficient *increases* on *increase* of the Q_1 . When, therefore, the same reaction is brought about without, and one with exceedingly little catalyst under for the rest identical circumstances, the catalysed reaction, which proceeds more quickly, will require a smaller heat of activation for its molecules, and possess a smaller coefficient of temperature than the not catalysed reaction, two conclusions which may be verified experimentally.

Briefly T.'s train of thought comes to this that he assumes that it is required both on formation and decomposition of molecules that they pass into a reactive form (not always atoms) with absorption of energy and that on collision of these active molecules the reaction always takes place. VAN 'T HOFF's reaction isochore being the starting point in TRAUTZ's theory, it is comprehensible that the stress has been laid on the changes of energy taking place in the reaction, and that the importance of the constant of integration is not sufficiently brought out. And yet it is clear on some consideration that the only thing required for a bi-molecular reaction is not a collision, but a collision at the right place (perhaps with the exception of very simple molecules). This favourable constellation which may be expressed in the form of a quantity of entropy, does not occur in the reaction isochore. Accordingly in TRAUTZ's theory changes of entropy in the reaction have only been considered in so far as the number of collisions are concerned.

That with by far the majority of the reactions change of the internal energy of the molecules is accompanied with change of the molecular entropy¹⁾, is not sufficiently taken into account in LEWIS's *theorie* either. There, too, it is assumed that before being able to react, every molecule must have a certain excess of energy, called by L *increment of energy*. This increment would be absorbed in

¹⁾ TRESLING, These Proc. Vol. XXIII, p. 143.

the form of infra-red radiation of very definite frequency, which radiation is present in the medium in virtue of its thermal condition. By the application of PLANCK'S law of the normal partition of energy, the density of radiation of this frequency can be calculated at every temperature, and from this the fraction of the molecules that are in reactive condition. LEWIS derives that the increment of energy E is equal to a quantum (of the absorbable type) per molecule.

$$E = Nh \sum v_{reagents}.$$

LEWIS derives for the constant of reaction of a bi-molecular reaction:

$$k = P_0 \sqrt{T} n_A^2 n_B^2 e^{-h(v_A + v_B)/kT}$$

in which $P_0 = \text{constant}$, $T = \text{absolute temp.}$, n_A and $n_B = \text{index of refraction of the substance } A \text{ resp. } B$, and $k = \text{gas constant per molecule}$. The formula shows very clearly the rapid increase of k on rise of temperature.

The nearer the value of the critical energy is to that of the mean energy per molecule, the greater will be the number of molecules becoming active per second, hence also the velocity of reaction, the same conclusion, therefore, to which TRAUTZ came. By taking the logarithm of the above formula, and differentiating this with respect to time, the following form results:

$$\frac{d \ln k}{dt} = \frac{Nh(v_A + v_B) + \frac{1}{2}RT}{RT^2} = \frac{E + \frac{1}{2}RT}{RT^2}$$

Of reactions which take place as much as possible under the same circumstances, only more slowly or more quickly (to be realized with little catalyst), the quicker reaction must have a smaller E according to the above, from which it then follows that $\frac{d \ln k}{dt}$ has become smaller, hence also the temperature coefficient of the reaction constant, for the temp.coef.

$$\frac{k_{T+10}}{k_T} = \frac{k_T + 10 \frac{dk}{dt}}{k_T} = 1 + 10 \frac{dk}{k_T dt} = 1 + 10 \frac{d \ln k}{dt}$$

LEWIS (like TRAUTZ) draws the conclusion that a strongly catalyzed reaction will indicate a decrease of the temperature coefficient compared with the same reaction weakly or not catalyzed.

On half thermodynamic, half kinetic grounds KOHNSTAMM and SCHEFFER have derived a relation between the velocities of reaction and the thermodynamic potentials of the substances participating in

a reaction. Starting from this SCHEFFER drew up a simple formula which agrees with a formula derived at about the same time in an entirely different way by MARCELIN, viz.:

$$\ln k = - \frac{E}{RT} + B,$$

in which E represents the difference of energy between the intermediate state which is rich in energy, and the mean condition of the reacting substances in the reaction, and B is a quantity which does not contain constants dependent on the nature of the substances, except the difference of entropy. This term takes the effective chance of collision into account. It follows from the formula that increase of the energy increment diminishes the velocity of reaction, increase of the difference of entropy on the other hand increases it. In contradistinction with the formulae discussed before, a catalyst need not necessarily decrease the energy increment; it is even possible that as a result the energy increment is increased, provided the increase of factor B more than neutralizes this unfavourable action. The increase of the energy increment means fewer active molecules, increase of B is equivalent to a more favourable chance of collision. It is, therefore, possible that the action of a catalyst would consist in this that though the threshold of energy should be raised, the number of favourable collisions has been so much increased that the reaction nevertheless proceeds more rapidly.

In the not catalysed reaction by no means every collision between active molecules would eventuate in a reaction. This is a priori sooner to be expected for complicated than for simple molecules; instances are, therefore, especially to be found in organic chemistry.

From increase of the energy-increment ensues increase of the temperature coefficient, hence the catalysed reaction can have a greater temperature coefficient than the not catalysed reaction. *Entirely in contradiction with TRAUTZ's and LEWIS's conclusions the catalysed reaction can have a temp. coef. and an energy increment which are greater than those of the same reaction without catalyst.*

Measurements of the velocity of one and the same reaction between complicated molecules with and without catalyst and at different temperatures might give a decision in favour of SCHEFFER's theory, if a reaction could be found which, catalysed, presented a greater temperature coefficient than not catalysed. As will be seen in what follows, this appeared to be the case in the acetylation of diphenylamin.

The reaction was carried out at 0°, 20°, 30°, 40°, and 50° C.

The excess of acetic acid anhydride was taken so great that the variations of concentration of this component could be neglected with respect to those of the component diphenylamin. Hence the reaction was pseudo-mono-molecular. Many catalysts were tried ¹⁾ before some substances were found which were not paralysed during the reaction; they were *p.* bromo-benzene-sulphonic acid and *p.* toluene-sulphonic acid.

The following tables give the observations from 0—50° without catalyst.

temp. 0° 1 mol diph. 12½ mol. anh.

| <i>t</i> | % converted | $\frac{K}{2.303}$ |
|----------|-------------|-------------------|
| 1.— uur | 1.1 | 0.0048 |
| 2.— " | 1.4 | 0.0031 |
| 3.— " | 2.1 | 0.0031 |
| 4.— " | 2.3 | 0.0025 |
| 5.— " | 2.4 | 0.0021 |
| 6.15 " | 3.0 | 0.0021 |

temp. 20° 1 mol. diph. 12½ mol anh.

| <i>t</i> | % converted | $\frac{K}{2.303}$ |
|----------|-------------|-------------------|
| 0.30 uur | 0.8 | 0.0069 |
| 1.30 " | 2.4 | 0.0070 |
| 2.30 " | 3.8 | 0.0067 |
| 3.30 " | 5.5 | 0.0070 |
| 4.30 " | 7.3 | 0.0073 |
| 6.— " | 9.1 | 0.0069 |

temp. 30° 1 mol diph. 12½ mol. anh.

| <i>t</i> | % converted | $\frac{K}{2.303}$ |
|----------|-------------|-------------------|
| 0.30 uur | 1.6 | 0.0127 |
| 1.01 " | 2.8 | 0.0121 |
| 2.— " | 5.5 | 0.0123 |
| 3.— " | 8.2 | 0.0124 |
| 4.— " | 10.8 | 0.0124 |
| 6.05 " | 16.3 | 0.0129 |

temp. 40° 1 mol. diph. 12½ mol anh.

| <i>t</i> | % converted | $\frac{K}{2.303}$ |
|----------|-------------|-------------------|
| 0.33 uur | 2.5 | 0.0220 |
| 0.58 " | 4.3 | 0.0208 |
| 2.— " | 8.9 | 0.0202 |
| 2.59 " | 12.9 | 0.0201 |
| 5.— " | 21.5 | 0.0210 |
| 7.— " | 29.0 | 0.0212 |

Taking into consideration that in the first table the converted quantities are so small, the most probable values of the reaction constants are respectively; 0,0021—0,0070—0,0124—0,0209 and 0,0384.

¹⁾ Diss. Delft 1922.

temp. 50° 1 mol. diph. 12½ mol. anh.

| t | % converted | $\frac{K}{2.303}$ |
|----------|-------------|-------------------|
| 0.30 uur | 4.4 | 0.0391 |
| 1. — " | 8.4 | 0.0381 |
| 2. — " | 15.2 | 0.0358 |
| 3. — " | 22.6 | 0.0371 |
| 5. — " | 36.1 | 0.0389 |
| 7. — " | 46.5 | 0.0388 |

The reaction constants of the catalysed reactions are recorded in the following table:

| | p.bromo-benzene-sulphonic ac. cat. | | p. toluene-sulphonic acid catal | |
|----------|------------------------------------|--------------|---------------------------------|--------------|
| | 0.00089 mol. | 0.00178 mol. | 0.00089 mol. | 0.00178 mol. |
| k_0 | 0.0018 | 0.0027 | 0.0021 | 0.0024 |
| k_{20} | 0.0102 | 0.0197 | 0.0105 | 0.0134 |
| k_{30} | 0.0243 | 0.0523 | 0.0235 | 0.0340 |
| k_{40} | 0.0598 | 0.143 | 0.0558 | 0.0819 |
| k_{50} | 0.153 | 0.383 | 0.123 | 0.194 |

It is remarkable that the activity of the catalyst decreases at low temperatures, and becomes about 0 at 0°. At lower temperature the catalyst is paralysed, to which we shall revert later on. The energy increment can be calculated from two observations by the aid of the formula $\ln \frac{k}{k_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T} \right)$. In the calculation of the energy-increment of the catalysed reactions it should be borne in mind that this must not be done in the usual way, if the measured reaction is a combination of two or more reactions taking place side by side ¹⁾. The hypothesis according to which it is assumed that with a small catalyst concentration, the number of collisions of the kind as occur in the non-catalysed reaction, remains the same, and that only another kind of collisions is added to them, is permissible in my opinion. In this case the measured constant of reaction

¹⁾ LACOMBLÉ, Diss. Leiden 1920, p. 80.

represents the sum of that of the non-catalysed and that of the purely catalysed reaction. In order to obtain the constants of the purely catalysed reactions, which are recorded in the above table, the reaction constants of the non-catalysed reactions must be subtracted from the measured ones. It has been tacitly assumed, what is, indeed, shown by the constancy of the measured reaction constants, that the two reactions proceeding side by side, are of the same order, as otherwise this operation is not allowed.

| | p. bromo benzene sulph. ac. catal. | | p. toluene sulphonic catal. | |
|----------|------------------------------------|--------------|-----------------------------|--------------|
| | 0.00089 mol. | 0.00178 mol. | 0.00089 mol. | 0.00178 mol. |
| k_0 | — | 0.0006 | — | 0.0003 |
| k_{20} | 0.0032 | 0.0127 | 0.0035 | 0.0064 |
| k_{30} | 0.0119 | 0.0399 | 0.0111 | 0.0216 |
| k_{40} | 0.0389 | 0.122 | 0.0349 | 0.0610 |
| k_{50} | 0.155 | 0.345 | 0.0846 | 0.156 |

The energy increment calculated from the 1st series of observations without catalyst, and from these 2nd, 3rd, 4th, and 5th series is respectively ± 10.000 calories — 23000 cal. — 20500 cal. — 20500 cal. — 20800 cal.

The acetylation of diphenylamin decides, therefore, in favour of SCHEFFER'S theory, as it would e.g. be entirely inexplicable according to LEWIS, why the sulphonic acid can act as catalyst, as the addition of this substance about doubles the energy-increment; the number of active molecules would, accordingly, be much smaller, hence also the number of effective collisions.

In the calculation of the factor B from SCHEFFER'S formula, it appears to be more than doubled by the catalyst. The favourable chance of collision has, therefore, been enlarged, notwithstanding the number of active molecules has become smaller. Hence if the conversion is to be increased, this smaller number of active molecules must collide more favourably. Accordingly every collision between molecules that are sufficiently rich in energy does not always eventuate in conversion, it is probably only a small percentage of them that enters into reaction.

One can form the following conception of this.

It is not immaterial what part of the acetic acid anhydride molecule impinges with the diphenylamin-molecule, nor with what part of the latter. The reactive molecule parts, in this case the

1st series.

| | E | B |
|----------------|-------|------|
| $k_{20} : k_0$ | 9600 | 12.3 |
| $k_{30} : k_0$ | 9800 | 12.7 |
| $k_{40} : k_0$ | 9800 | 12.6 |
| $k_{50} : k_0$ | 10200 | 13.4 |

2nd series.

| | E | B |
|-------------------|-------|------|
| $k_{30} : k_{20}$ | 23200 | 34.7 |
| $k_{40} : k_{30}$ | 23000 | 34.4 |
| $k_{50} : k_{40}$ | 22600 | 33.8 |

3rd series.

| | E | B |
|-------------------|-------|------|
| $k_{30} : k_{20}$ | 20200 | 31.1 |
| $k_{40} : k_{30}$ | 20800 | 32.0 |
| $k_{50} : k_{40}$ | 20800 | 32.1 |

4th series.

| | E | B |
|-------------------|-------|------|
| $k_{30} : k_{20}$ | 20400 | 30.1 |
| $k_{40} : k_{30}$ | 21000 | 31.1 |
| $k_{50} : k_{40}$ | 20200 | 29.8 |

5th series.

| | E | B |
|-------------------|-------|------|
| $k_{30} : k_{20}$ | 21600 | 32.7 |
| $k_{40} : k_{30}$ | 20800 | 31.3 |
| $k_{50} : k_{40}$ | 20200 | 30.4 |

oxygen bridge of the anhydride and the aminohydrogen of the amin, must be in each other's immediate neighbourhood. In a substance which exercises an attraction on these two parts, these molecule parts will be turned towards each other at a collision of the three molecules (more probable is a collision of a molecule with the complex of the two others). The sulphonic acids used certainly exert an attraction on the amino hydrogen, and most likely also on the bridge oxygen, because sulphuric acid impinges with the anhydride at that place, and the sulphon group is the active component in both substances. In my opinion the catalytic action of sulphonic acid is for the greater part due to its *directive* action, and it owes this directive action to its affinity towards the reaction components, as BÖESEKEN's dislocation theory demands for every catalyst, without this affinity leading to such a firm bond, that the affinity, hence also the directive action on the other kind of molecule, would be eliminated.

Against these conclusions the question might be raised whether the measured temperature coefficient represents indeed the real one. The nature of the catalyst leads to the supposition that a part of the sulphonic acid is bound to the diphenylamin resp. anhydride (or both), and that this might not be active (or much less so). On rise of temperature a stronger dissociation would appear in the components, hence more free (i.e. more active) catalyst would be present. Then

the measured temp. coeff. is not $= \frac{k_{T+10}}{k_T}$, but $= \frac{k_{T+10}}{k_T} \times \frac{c_{cat T+10}}{c_{cat T}}$. Accordingly the real temp. coef. would be smaller than the measured one.

Let us suppose the bound catalyst to be totally inactive, and the true temp. coef. to have remained of the same value as was found in the non-catalysed reaction. The measured temp. coef. $= 3 = 1,8 \times \frac{c'_{cat}}{c_{cat}}$, from which $\frac{c'_{cat}}{c_{cat}} = 1,67$, in other words one is confronted by the question whether it is possible that in the neighbourhood of room temperature the concentration of the components increases by 67 % per 10° increase of temperature.

Let us take 300° and 310° absolute for the two temperatures, 0,1111 as constant of equilibrium at 300° (hence 90 % bound cat, 10 % free cat), and let us put the heat of dissociation $= 5000$ cal, a heat which may be called normal.

$$K_{300} = \frac{10 \times c_A}{90} \quad K_{310} = \frac{x \times c'_A}{100-x}$$

in which $c_A = c'_A$ may be put:

$$\frac{K_{310}}{K_{300}} = \frac{x}{100-x} \cdot 9.$$

It follows from the reaction-isochore that:

$$\log \frac{K_{310}}{K_{300}} = \frac{Q}{4,571} \cdot \frac{T_{310} - T_{300}}{T_{310} T_{300}} = \frac{5000}{4,571} \cdot \frac{10}{93000} = 0,1176$$

from which:

$$\frac{K_{310}}{K_{300}} = 1,31 = \frac{x}{100-x} \cdot 9$$

from which:

$$x = 12,7 \quad \text{and} \quad \frac{c'_{cat}}{c_{cat}} = 1,27.$$

Hence even in the most unfavourable case conceivable that the bound catalyst would be totally inactive, the increasing dissociation per 10° increase of temperature is only able to account for a small part of the increase of the temp. coef. of the catalysed reaction above that of the non-catalysed reaction.

SCHAEFFER pointed out that in many cases the E may be put practically constant over a limited range of temperature, and that in this case B is also pretty well constant. If the region from 20°—50° lies within this limited range, the values of $\ln k$ drawn

as function of $\frac{1}{T}$, must lie on a straight line, for every equation of the form $y = mx + b$ represents a straight line. Expressed in a graphical representation this appears really to be the case¹⁾, and the course of the lines suggests that the energy-increment is little, if at all, dependent on the quantity of added catalyst. The values of $\ln k$ at 0° fall outside the straight line in the catalysed reactions.

As on account of the slight velocity of the reaction at 0° the observations need not be very accurate, I repeated two measurements at 0°, viz. of the non-catalysed reaction, and of that with 0,00178 mol. p. bromobenzene sulphonic acid. I extended the observations over fully two days instead of over seven hours.

temp. 0° 1 mol. diph. 12½ mol. anh.

| t | % converted | $\frac{K}{2.303}$ |
|-----------|-------------|-------------------|
| 21.55 uur | 8.0 | 0.00165 |
| 28.26 > | 10.1 | 0.00162 |
| 44.55 > | 14.5 | 0.00152 |
| 52.52 > | 17.6 | 0.00159 |

temp. 0° 1 mol. diph. 12½ mol. anh.
0.00178 mol. acid.

| t | % converted | $\frac{K}{2.303}$ |
|-----------|-------------|-------------------|
| 21 48 uur | 10.3 | 0.00216 |
| 28,19 > | 12.9 | 0.00212 |
| 44.48 > | 19.4 | 0.00210 |
| 52.44 > | 23.8 | 0.00224 |
| 75.46 > | 32.3 | 0.00226 |

Though the values which I found, were indeed lower, the constant of the purely catalysed reaction appeared to have the same value as was determined in former experiments, viz. $0,00218 - 0,00160 = 0,00058$ (found formerly = 0,0006).

To be expected was a value $\pm \frac{0,0127}{(3,1)^2} = \pm 0,00132$, hence for the gross catalysed reaction $0,00132 + 0,00160 = \pm 0,0029$; a value that exceeds the error of observation many times.

In FeCl_3 I think I have found a catalyst which is catalytically active undiminished down to 0°. As these experiments have not yet been completed, they will be discussed in a later publication; I may conclude from the experiments already made that also ferri-chloride enlarges the "hill" of energy and that accordingly also this catalytic action can alone be explained by the aid of SCHEFFER'S theory.

¹⁾ Diss. Delft 1922.

Chemistry. — “*The Dislocation Theory of Catalysis.*” By Prof. J. BÖESEKEN.

(Communicated at the meeting of May 27, 1922).

The explanation of the catalytic phenomena has always presented great difficulties, and has never been satisfactory as yet, because the cause of changes of reaction-velocity was to be ascertained without there seeming to be a clear relation between the velocity of reaction and the quantity of energy that came into play.

Before the catalytic phenomena had been brought in connection with the conception of free energy, satisfaction might be found in establishing the fact that one or more intermediate reactions took place, which together proceeded more rapidly than the reaction without catalyst.

And it is still possible to be satisfied with such an explanation when it can also be shown that the catalyst in quantity and quality is eventually regained unchanged from the reaction mass.

It should, however, be fully realized that no answer is given to the question why these intermediate reactions proceed more rapidly than the principal reaction.

This is the more striking, because in these intermediate reactions the catalyst disappears from the reaction-mass at least temporarily and partially. I have, therefore, pointed out that the ideal catalysts are exactly those that are *not* fixed in intermediate reactions, and that the *real catalysis* is the interaction between the catalyst and the molecules, which has nothing to do with the formation of a compound as such.

This interaction, which I have called *dislocation*, may be seen as a change of the paths of the electrons; it is very well possible that it cannot take place until the catalyst has formed a compound with the molecules, but at any rate it must be possible to show it in some way or other and to express it in a mathematical form.

On one side it is therefore necessary to form a clear conception of the dislocation, on the other side the modifications which take place in the thermodynamic relations through the presence of a catalyst and to which the changes of the reaction velocities respond, must be fixed in a mathematical formula by establishing a connec-

tion between the reaction velocities and the thermodynamic relations.

As regards the former, *in the oxidation of alcohols with cooperation of aromatic ketones activated by light* I have found a reaction, in which the catalysis proper (the dislocation) could be sharply distinguished from the formation of a compound between catalyst and the molecules present.¹⁾

When an alcoholic solution of benzophenon, which is kept saturate with oxygen, is exposed to violet light, the alcohol is oxidized to aldehyde and water, the ketone remaining unchanged.

A closer study brought to light that above a certain concentration of the ketone the velocity of reaction became independent of this concentration, and further that it was proportional to the *square* of the intensity of the light and to the first power of the conc. of the alcohol.

This may be explained as follows:

The ketone absorbs part of the light and is activated by it. According to the laws of absorption the quantity of active ketone will be proportional to:

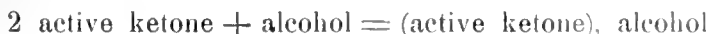
$$I(1 - e^{-kcd}) \text{ in which } k = \text{absorption coefficient}$$

$$c = \text{concentration ketone}$$

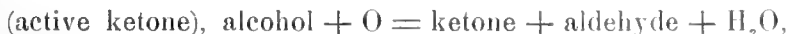
$$d = \text{thickness of layer}$$

Ie^{-kcd} is the light that is transmitted. If k , c , and d are pretty great, this is very little, and all the light is absorbed. The quantity of activated ketone then becomes proportional to I and independent of c , its concentration.

When we assume that among others the two following processes take place:



and



the former of which proceeds much more slowly than the latter, the oxygen absorption (which was measured) will be determined by the first process, the velocity of formation of the ternary compound. This velocity of reaction must then be proportional to the square of I and to the concentration of the alcohol.

I will not enter here into a fuller discussion how this might be proved in different other ways²⁾. The whole process can now be described as follows:

Under the influence of the light there is suddenly formed a

¹⁾ Recueil **40**, 433—445.

²⁾ l. c. p. 439—442.

quantity of photo-ketone $= kI (1 - e^{-kadt})$ approaching to kI .

I. ketone + light = photo-ketone;

as this quantity is formed at the moment that the solution is illuminated, it is as if with the velocity of light a plate of a catalyst slides on the light side of some vessel or other, in which the solution is put.

Then the reaction takes place the velocity of which regulates the process: the meeting of the alcohol molecules and those of the photo-ketone:

II. 2 photo-ketone + alcohol = (photo-ketone), alcohol.

By this meeting two H-atoms of the alcohol are activated:

III. (photo-ketone), alcohol \rightarrow [(photo-ketone), active alcohol].

This process, which probably takes place with the velocity of light, is the real catalysis, the dislocation.

The alcohol-molecules are enabled to react with the oxygen according to the scheme:

IV. 2 [(photo-ketone) active alcohol] + O₂ =
4 ketone + 2 aldehyde + 2H₂O,

which last process also takes place with great velocity.

We see that the actual catalysis has to do with the formation of the ternary compound only in so far as the photo-activity of the C=O-groups of the ketone can be transferred to the H-atoms of the alcohol. Here the distinction of the catalysis and of the formation of the compound is, indeed, very clear, for the ternary compound is also formed in the dark, and then there is no question of any catalytic action.

When the photo-ketone is thought replaced by an ordinary catalyst, e. g. a plate of paladium, it is clear that the combining of this metal with the alcohol is not the essential part of the catalysis, but what happens with the alcohol molecules at the moment that the atoms *Pd* get into contact with them, through which two of the H-atoms are activated. This the paladium can do by itself, without being activated by a stimulus from outside.

It appeared from the light-investigation that the oxidation of the activated alcohol molecules took place very rapidly. This will as a rule also be the case in the ordinary catalysis, but this velocity can be different for each case.

If, however, a catalyst in very small quantities is to accelerate a given reaction considerably, every contact of its molecules with those of the substance that is to be activated, must give rise to a dislocation that sets in very rapidly.

It is clear that this can hardly take place otherwise than on *intimate* contact, and here the significance of the formation of a compound between catalyst and the molecules to be activated, even though it be one that can very easily be dissociated, comes to the fore. In the light investigation it was only the primary and secondary alcohols that were easily oxidized, and *not* the hydrogen itself and a number of hydrogen compounds, evidently because the former *could*, the latter *could not* be attached by the ketone.

As has been said in the introduction, not only must the conception of dislocation be defined more closely, but it must also be tried to find a mathematical form for it through the consideration of the thermo-dynamic and kinetic relations.

Of late years many scientists have occupied themselves with studies of the reaction velocities, which are also the subject of this investigation. We may mention the names of TRAUTZ, MARCELIN, LEWIS, PERRIN, and SCHEFFER¹⁾.

It seems to me that SCHEFFER's considerations have the greatest value for the knowledge of the significance of the *dislocation*, because there the question is put whether a formula for the phenomena of diffusion (drawn up by KOHNSTAMM) is also valid for the description of the reaction velocities, and this question is answered in an affirmative sense.

For the chemical phenomena are essentially phenomena of diffusion in which particularities will occur only in the partial mutual penetration of atoms and molecules. In SCHEFFER's theoretical research the significance of these particularities, which were represented in the form of thermo-dynamic relations of the "intermediate states", was clear. It is self-evident that it is exactly *these* relations which are modified by the catalyst, and that comparison of these relations without and with the catalyst, must lead to a standard of the *dislocation*.

SCHEFFER's simple equation of the relation between the reaction constant, the quantities in question, and the temperature is:

$$\ln k = -\frac{E_t - E}{RT} + B.$$

In this $E_t - E$ is a measure for the difference of energy between the reacting substances and the intermediate state at the reaction²⁾, B contains the differences of entropy and constants

¹⁾ These Proceedings Vol. XIII, p. 789 and Vol. XV, p. 1109.

²⁾ It is the energy which a gram-molecule requires above the mean energy at the temp. T in order to react, and which is sometimes expressed by the name of *energy-increment*.

which do not depend on the nature of the reacting substances.

As a difference of entropy is a measure for a greater or less probability, and as this probability must refer to the reaction setting in more or less easily, both this difference of energy and this probability can be calculated by the aid of this formula from two observations at different temperatures, and by carrying out this calculation with and without a catalyst it can be ascertained in what way these two relations are modified by the catalyst.

As appears from the following communication, this calculation has been applied by E. VAN THIEL to the acetylation of diphenylamin with acetic acid anhydride both in presence of *p*-bromo (methyl)-phenylsulphonic acid as catalyst and without it, and the remarkable result has been obtained that in the presence of a catalyst the factor ($E_c - E$) is about doubled, B becoming also considerably larger. The conclusion may be drawn from this that in this case by the addition of a catalyst more than double the energy is, indeed, required to cause the molecules to react than without it, but that this unfavourable factor is far more than compensated by the so much greater probability for the setting in of the reaction in the presence of the catalyst.

In his address at the spring meeting of the Ned. Chem. Ver. (Dutch Chemical Association) of April 20 1922 SCHEFFER expressed this as follows: the hill of energy that is to be surmounted becomes, indeed, higher, but the road across it, becomes very much broader.

Though it may be more or less a coincidence that in the case examined by VAN THIEL the hill of energy is so much higher in the presence of a catalyst than without it, it is yet the confirmation of my view that the formation of a compound between the catalyst and the substances to be activated sooner hampers than promotes the reaction, and that the catalyst performs its accelerating action *not by combining* with these molecules, but *in spite* of this combination.

The acceleration of the reaction takes place because simultaneously with the formation of this compound a change of condition sets in, the *dislocation*, in which the conditions for the occurrence of the reaction become so much more favourable. The conception of dislocation has found a confirmation through SCHEFFER's theoretical investigation, and a measure in the variation of the quantity B of his formula.

In conclusion it may still be pointed out that the thermo-dynamic-kinetic considerations have not brought the question *why* a catalyst creates favourable conditions, nearer to its solution. The possibility may be considered of the molecules assuming a certain position,

which causes the collisions to take place on the reactive parts of the molecules (VAN THIEL, see following communication), or it may be supposed that the reactive surface is enlarged, etc. etc. It is certain that these changes of position or of form must take place very rapidly, and the catalyst must be under very favourable conditions with regard to the molecules that are to be activated, which can hardly be imagined in another way than ensuing from a chemical affinity, which leads to dissociation equilibria that are established very rapidly.

Delft, May 1922.

Botany. — “*The disappearance of the diploid and triploid magni-coronate narcissi from the larger cultures and the appearance in their place of tetraploid forms*”. By DR. W. E. DE MOL.
(Communicated by Prof. G. VAN ITERSON JR.).

(Communicated at the meeting of June 24, 1922).

I. *Introduction.*

Simultaneously with my investigations into the causes which lead to the immense variety of size and form in the *Hyacinthus orientalis* in Holland, I commenced a similar research with respect to the species of narcissi and narcissus-hybrids under cultivation. These comparative researches have led to some noteworthy results. One conclusion I arrived at was that, as is the case with *Hyacinthus orientalis*, the remarkable size of the bulbs, leaves and flowers which characterize the bastards of *Narcissus Pseudonarcissus* now cultivated, correspond mainly with the number of chromosomes of which, according to my cytological observations, the somatic nuclei consist.

This feature which, as far as I have been able to observe, occurs in *Hyacinthus orientalis* only in the Dutch cultures, is found both in England and in the Netherlands in *Narcissus Pseudonarcissus*, and is more pronounced than in the hyacinth. In the latter there are probably no tetraploid plants yet, whereas there are several in the *Narcissus Pseudonarcissus*.

II. *Some results of the cytological investigation.*

The preparations which I used in my cytological researches were made in the same way as those for hyacinths. The thickness of the sections is 10 or 15 μ according to the size of the cells and nuclei.

ASCHERSON and GRAEBNER (1) give the *Magnicoronati* as the 1st section of the sub-genus *Eunarcissus*. This section is entirely formed by the class *N. Pseudonarcissus*, which they divide into 2 sub-classes, *N. festalis* and *N. minor*. For convenience sake in describing the varieties studied, I shall keep to this classification, except that I shall place the sub-division *N. minor* first.

1. *N. minor.*

The somatic nuclei of *N. minor* (the type), *N. nanus*, *N. minimus* and *N. cyclamineus* (which is best classed with the sub-species

N. minor) consist of 14 cylindrical chromosomes, 10 long ones and 10 short ones.

2. *N. festalis*.

a. *Diploid varieties*.

The somatic nuclei of *N. muticus* (syn. *abscissus*), *Capax plenus* (which perhaps ought to be classed under *N. minor*), *Telamonius plenus* (Double Sion, Wilmer's great double golden yellow Daffodil), large old double yellow trumpet Daffodil) also comprise 14 chromosomes which I cannot distinguish from the former ones.

b. *Heteroploid varieties*.

N. Johnstoni Queen of Spain possesses somatic nuclei with 20 chromosomes. In *Maximus* and *Golden Spur* these nuclei consist of 21 chromosomes, so that judging from the number these varieties are triploid.

The nuclei of *Bicolor Victoria* and *Buttonhole* (obtained from *Bicolor Victoria* by budvariation) contain 22 chromosomes. The chromosomes-garniture of both forms is the same.

The varieties *King Alfred* and *van Waveren's Giant* are, to judge from the number of chromosomes, tetraploid, for here the somatic nuclei consist of 28 chromosomes.

In all the 14 forms above-mentioned and examined, the chromosomes — both long ones and short ones — correspond in size and shape. The diploid nuclei always consist of 10 longer and 4 shorter chromosomes. I cannot yet state the exact number of long and short chromosomes of the nuclei of the heteroploid forms. To do this it is necessary to examine over 3000 good sections with dividing nuclei; I have now examined this number. Probably the longer and shorter chromosomes do not differ in length and breadth from each other, and as in *Hyacinthus orientalis* the pairs of long and short chromosomes will not be distinguishable from each other by any characteristic constant difference in form, as is described of *N. poeticus* by STOMPS (3).

III. *Self-pollination in diploid, triploid and tetraploid forms*.

In contrast with *Hyacinthus orientalis*, in such categories as can be distinguished cytologically, self-pollination yields good practical results. From the few seeds of the diploid *N. minimus, minor, cyclamineus* (and *N. triandrus albus*), taken in 1913, 1914 and 1915, I have reared plants which are not distinguishable in bulb leaf and flower from the parent species.

In the case of the triploid *Golden Spur* self-pollination yielded

plants which in form and size differed from each other and from the parent species.

By means of self-pollination of the tetraploid *King Alfred* I got hundreds of seeds in 1914 and 1915. In 1916 I had about 1400 small bulbs. This spring 50 flowers came out, which differed greatly in form and size from each other and from *King Alfred*. Most of them were smaller than the parent species. The tetraploid *Van Waveren's Giant* can also be self-pollinated successfully.

IV. Conclusion.

1. Of the variety *Maximus* which I examined we are aware that it was already known in 1600, from which it may be inferred that even three hundred years ago there was triploidity in the magnicoronate narcissi. Triploidity must have commenced with the wild species or those again run wild, as the above-mentioned variety and *Golden Spur* (first cultivated between 1885 and 1888) were probably not obtained in nurseries (see 6). Regarding the wild variety of *N. Johnstoni Queen of Spain*, BAKER assumes that this is a hybrid between *N. Pseudonarcissus* and *N. triandrus*. If this is correct — and the bastards cultivated of these two varieties leave no room for doubt — this variety of *Queen of Spain* is in all probability a bastard between a heteroploid form of *N. Pseudonarcissus* and *N. triandrus*, as my experience shows the latter to be diploid and to possess the same chromosome garniture as the diploid narcissi already mentioned.

2. If we keep to the classification of ASCHERSON and GRAEBNER we shall see that the feature of the heteroploidity was first seen in the genus or group of *N. Pseudonarcissus festalis major*, the diversity which by hybridization has principally yielded the large garden forms of the present day.

It is very interesting how the increase in the size of these varieties now cultivated can be traced. Up till 1885 — the diploid varieties were chiefly grown. The culture of the *Golden Spur* marks the beginning of the era of the triploid garden forms.

Bastards between *Maximus*, *Golden Spur* and other valuable kinds are grown, with the result that larger specimens have been obtained, of which *King Alfred* (England; firm of KENDALL) is the finest. From this dates the advent of the tetraploid varieties (1899).

Just as the climax in point of size of the diploids seems to have been reached in *Telamonius plenus*, and of the triploids in *Golden Spur*, the culminating point among the tetraploid forms seems to have been reached in *Van Waveren's Giant*. Nevertheless this

has been surpassed again by magnicoronate narcissi, the dimensions of which are greater in one or two respects (e. g. *Early Giant*, *Apotheose*, *Ajax Grand Vizier*, *Imperator* and *Mammoth*; (see for this the "Weekblad voor Bloembollencultuur", 32nd. Year, 1922, Nos. 85, 87, 89, 91 and 93), so that we may suppose that there are already hypertetraploid forms. In this connection the significant question arises as to whether the number of chromosomes may go on increasing indefinitely. Or, in other words: Is there any limit, and if so, where?

The same question has been asked by BEUMER with regard to the increasing size. ("Weekblad" n°. 101). In the following table some of the measurements are given in millimetres; they are nearly the same as those given in the publication of SYDENHAM (4), with the exception of those for *Mammoth*, which are mentioned in "Weekblad", n°. 93.

| Name of variety | Diameter perianth | Tepals | | Paracorolla | | Number of chromosomes |
|----------------------------|-------------------|--------|---------|-------------|---------|-----------------------|
| | | length | breadth | length | breadth | |
| <i>Queen of Spain</i> | 82 | 35 | 15 | 28 | 28 | 20 |
| <i>Bicolor Victoria</i> | 101 | 44 | 35 | 44 | 44 | 22 |
| <i>King Alfred</i> | 107 | 40 | 28 | 44 | 50 | 28 |
| <i>Van Waveren's Giant</i> | 127 | 50 | 38 | 50 | 50 | 28 |
| <i>Mammoth</i> | 140 | ? | ? | 55 | 60 | ? |

3. It goes without saying that I cannot now sacrifice the plants that I have obtained from *King Alfred* and *Golden Spur* for a cytological examination. But even without this examination it seems to me highly probable, especially when I test these observations by those conducted by WINKLER with *Solanum* (5) and those of VAN OVEREEM with *Oenothera* (2), that these conspicuous differences in form and size are primarily due to an unequal distribution of the chromosomes in the reduction-dividing of which an unequal combination of the sex nuclei is the inevitable result.

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*Plant physiological Laboratory of Prof. ED. VERSCHAFFELT,
Hortus Botanicus, at Amsterdam.*

Mathematics. — “Numbers of Circles Touching Plane Curves Defined by Representation on Point Space.” By L. J. SMID JR. (Communicated by Prof. HENDRIK DE VRIES),

(Communicated at the meeting of June 24, 1922).

The circles of a plane (degenerations included) may be represented without exception through a one-one representation on the points of a projective space. (R. MEHMKE, *Zeitschrift für Mathematik und Physik* 24 (1879)). We can arrive at it among others in the following way:

Let W be an umbilical point of a quadric O^2 and let w be the tangent plane at that point, B a plane, parallel to w . A plane section of O^2 with its pole relative to O^2 is projected out of W on B as a circle with its centre, and inversely. We consider this pole as the image of the circle.

As a special case we may take for O^2 a quadric of revolution of which W is a vertex. If moreover O^2 is a sphere, we get the representation of Prof. JAN DE VRIES (*Verhandelingen* 29); if W moves to infinity it becomes the representation of Dr. K. W. WALSTRA (*Verhandelingen* 25).

Prof. H. K. DE VRIES has studied cyclographically the circles touching a curve C in B of the order μ , the class r , passing ε times through both the circle points (with ε different tangents in finite space which cut C at those points in $\varepsilon + 1$ points), touching the line g_∞ singly in σ different points and having further no other singularities than δ nodes, \varkappa cusps, τ bi-tangents and ι inflexional tangents (*Verhandelingen* 8).

We arrive at the same results through the above mentioned representation. We shall only consider the principal ones.

The curve C is projected out of W on O^2 as a curve consisting of the two generatrices through W , counted ε times, and a curve k of the order $n = 2\mu - 2\varepsilon$ passing $(\mu - 2\varepsilon)$ -times through W . σ pairs of tangents at W coincide, because the parabolic branches of C give rise to cusps of k in W . Further k has δ nodes, \varkappa cusps and $(\mu - \varepsilon)(\mu - \varepsilon - 1)$ apparent nodes and no stationary tangents. By means of PLÜCKER'S formulas we find other numbers characteristic of k .

From the nature of the representation there follows that the points of the surface L of the tangents of k represent the circles cutting C at right angles. The tangent planes to O^2 at the points of k

envelop a developable surface K the points of which represent the circles touching C and the points of the cuspidal curve l of K represent the osculation circles of C . There exists a polar relation between the points, tangents, and planes of osculation of k and the planes of osculation, tangents, and points of l . Out of the characteristic numbers of k and L we find accordingly through dualisation the characteristic numbers of l and K , for instance:

$$\begin{aligned} \text{Order of } l: & m = \iota + 3\mu - 6\varepsilon - 2\sigma \\ \text{Order of } K: & r = 2\mu + \nu - 4\varepsilon - \sigma \\ \text{Cusps of } l: & \beta = 5\mu - 3\nu + 3\iota - 8\varepsilon - 3\sigma \\ \text{Order of the nodal curve of } K: & x = \frac{1}{2}\{(2\mu + \nu - 4\varepsilon - \sigma)^2 - 13\mu - \nu \\ & - 3\iota + 24\varepsilon + 7\sigma\}. \end{aligned}$$

From this follows among others:

To a given pencil there belong r tangent circles of C , but to a concentric pencil only $r - (\mu - 2\varepsilon)$ in finite space (class of the evolute). If we have 3 curves C_1, C_2, C_3 , the surfaces K_1, K_2, K_3 , have in all r_1, r_2, r_3 points in common, of which however there lie $4(\mu_1 - 2\varepsilon_1)(\mu_2 - 2\varepsilon_2)(\mu_3 - 2\varepsilon_3)$ in W . The rest is the number of circles touching the 3 curves.

Through a given point there pass m osculating circles of C . The projection of l out of W on B is the evolute; l passes σ times through W , hence the order of the evolute is $m - \sigma$. The evolute has β cusps (vertices of C) in finite space and moreover $\mu - 2\varepsilon - 2\sigma$ at infinity, arising because $\mu - 2\varepsilon - 2\sigma$ tangents of l pass through W , lie in w and have their points of contact outside W .

Through a point there pass x circles touching C twice. The locus of the centres of these bi-tangent circles is the projection of the nodal curve of K . This curve however passes $s = (\mu - 2\varepsilon)(\mu - 2\varepsilon - 1) - \sigma$ times through W , so that the order of the projection is only $x - s$.

The number of tangents to l cutting l once more, is $\gamma = rm + 12r - 14m - 6n$. Of these $2\sigma(\mu - 2\varepsilon - 2)$ lie in w through W . The rest gives the number of circles of curvature touching C once more.

The number of triple points of K is:

$$t = \frac{1}{6}\{r^3 - 3r(r + n + 3m) - 58r + 42n + 78m\}.$$

Of these however

$$4 \frac{(\mu - 2\varepsilon)(\mu - 2\varepsilon - 1)(\mu - 2\varepsilon - 2)}{1 \cdot 2 \cdot 3} - 2\sigma(\mu - 2\varepsilon - 2)$$

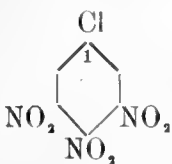
lie in W . The rest gives the number of circles touching C thrice.

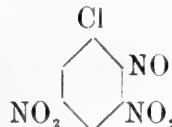
If we work out these formulas they get the same form as those of Prof. DE VRIES as is to be expected.

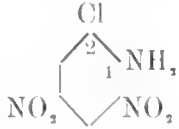
Chemistry. — “*Monochloro-trinitrobenzenes.*” By Prof. A. F. HOLLEMAN.

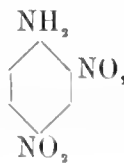
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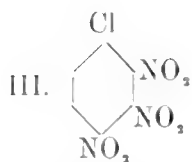
So far only two of the six possible isomers were known, viz. picrylchloride and a product obtained by NIETZKI (see below). For an inquiry into the replaceability of substituents it was required to prepare also the other four isomers. I have only been able so far to lay hands on three, and without doubt I should have waited with the publication of my results till the whole investigation had been completed, if I had not happened to hear that also others are engaged in a study of the same subject.

I.  *1-chloro-3, 4, 5-trinitrobenzene.* This compound is easily accessible; it is indeed surprising that it has not been known long since. The starting-point for its preparation is chlorodinitraniline 1, 4, 2, 6, in which NO₂ was substituted for the NH₂ group according to the method of KÖRNER and CONTARDI. The yield of raw compound amounts to 70% of the theory, and there is only little loss in the purification. The substance may be recrystallized from benzene. It then melts at 168°. Large yellow crystals.

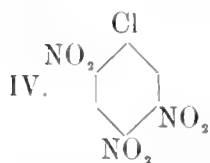
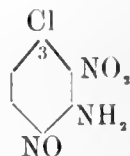
II.  *1-chloro-2, 3, 5-trinitrobenzene.* This compound is formed on very energetic nitration of 1-chloro-2,3-dinitrobenzene with a mixture of fuming nitric acid and oleum of 50%. The heating of 160—170° is continued for 5 hours. When the mixture is poured out into water, an oil is obtained, in which crystals are formed after some time. By centrifugation these are separated and then recrystallized from alcohol. Melting-point 106°. The structure of this compound was verified by a treatment with alcoholic ammonia, through which 2-chloro-4,6-dinitraniline is obtained, melting-point 159°. This compound is known. Much more easily, however, than according to the methods used up to now it could be prepared by chlorination of

 2-4-dinitraniline with KClO₃. The entrance of a NO₂-group chloro-2,3-dinitrobenzene is group takes a position at *m* with regard to a nitro-group.

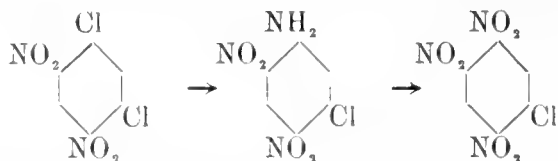




1-chloro-2,3,4-trinitrobenzene. In the nitration of 1-chloro-2,3-dinitrobenzene by the method given under II, the oil from which II was crystallized contains this third isomer. When the oil stands for a long time, the isomer crystallizes out of it in colourless needles of the melting-point of 69°. They are purified by recrystallization from alcohol. The structure of this compound can also be determined by treatment with alcoholic ammonia. If the action of the ammonia is allowed to last only for a short time, only one of the nitro-groups is replaced by NH₂. The aniline formed is 3-chloro-2,6-dinitraniline for 1-chloro-2,4-dinitrobenzene is obtained from it by deamidation. This aniline has the melting-point 112°; it was unknown up to now.



1-chloro-3,4,6-trinitrobenzene. This compound was already prepared by NIETZKI by nitration of 1-chloro-3,4-dinitrobenzene. On repetition of his experiments it appeared to me that the yield was small, and especially very uncertain, because either the nitration remains incomplete, or the reaction is so violent that total destruction ensues. It is therefore, better to proceed as follows:



The substitution of NH₂ for Cl takes place in alcoholic solution on the waterbath with addition of gaseous ammonia, till a test-sample shows the correct melting-point of 174°. According to KÖRNER and CONTARDI NO₂ can then be substituted for NH₂. The crude product is coloured black. It can be purified by boiling with nitric acid 1.4, followed by recrystallisation from alcohol. The melting-point is 116°, as has been given by NIETZKI.

No method of preparation has as yet been found for the last isomer, the 1-chloro-2,3,6-trinitrobenzene; probably it is also present in the oil obtained in the nitration of 1-chloro-2,3-dinitrobenzene.

Amsterdam, June 1922. *Org. Chem. Lab. of the University.*

Physiology. — “*On Respiratory Oscillations in the Galvanogram of Man.*” By A. A. WEINBERG. (Communicated by Prof. E. D. WIERSMA.)

(Communicated at the meeting of June 24, 1922).

An inquiry into the psycho-physiological significance of the psychogalvanic reflex, which will ere long be reported in detail, gave rise to the question whether the respiratory arrhythmiae in the plethysmogram which result from a predominating influence of the sympathetic nerve, or of the vagus, on the heart¹⁾, may be attended with oscillations in the so-called rest-current of the galvanogram. In order to set this question at rest the following experimental arrangement was set up.

Our subjects were healthy individuals from 20 to 40 years of age, without any anomalies of the heart or the urine. The current was lead off by non-polarizable electrodes from the baths of a four-cell bath, and was registered with the quick sensitive electrocardiograph of SIEMENS and HALSKE. The non-polarizable electrodes consisted of porous pots filled with a saturated zinc-sulphate solution, with a zinc rod. These pots were placed in the baths, which contained a physiological NaCl-solution heated to body-temperature. The current was recorded by the compensation-method, as the condensator-method¹⁾ does not enable us to observe the slow oscillations of the current. The sensitivity of the galvanometer, which was controlled for each separate registration, amounted to 4 m.V. per cm. For convenience's sake I selected the three leads which are generally used for taking an electrocardiogram. The method of EINTHOVEN and ROOS²⁾, which implies the use of fingerelectrodes and has the advantage of not being complicated by the electrocardiogram, did not yield satisfactory results in these experiments. For further particulars of the procedure of the experiments I refer the reader to my article in the “*Nederlandsche Tijdschrift voor Geneeskunde*” (l.c.).

With all the subjects thus far examined in this way (fifteen) respiratory oscillations were noticeable in the level of the electric curve. The only requisite was that the subjects had to be in a condition of perfect quiescence, and that their attention be not diverted by anything. Directly when they were more or less pre-

¹⁾ A. A. WEINBERG, *Ned. Tijdschrift v. Geneeskunde*; 66, II, 343, 1922.

²⁾ W. EINTHOVEN and J. ROOS, *Pflüger's Archiv*; 189, 126, 1921.

occupied, either in consequence of the experiment or through the after-effect of emotional occurrences, the respiratory oscillations disappeared from the galvanogram, while in the case of still intenser preoccupation other modifications in the level of the curve appeared, which were independent of respiration. All these modifications in the shape of the galvanic curve run parallel with the oscillations in the level of the plethysmogram, either in the same or in the opposite direction. Curve I is an illustration of the respiratory oscillations in the galvanogram.

The following objections may be raised to the hypothesis that these oscillations are connected with the respiratory oscillations in the equilibrium between the sympathetic and the parasympathetic (vagus resp.) nervous system :

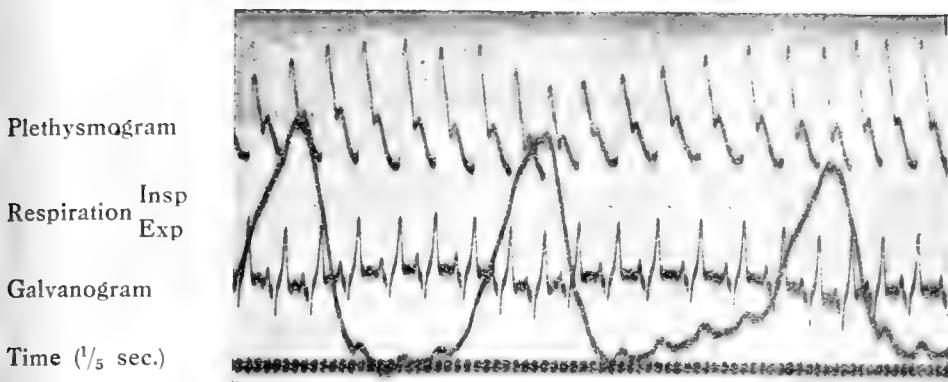
a. The oscillations are effected by the movements of the respiration-muscles.

b. They are caused by the changes in the electrical resistance which are brought about by rhythmic movements of the arm during respiration.

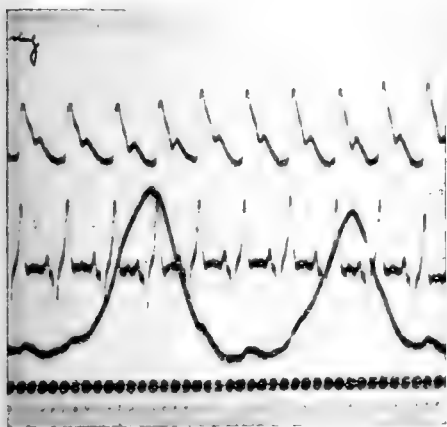
c. They are caused by the respiratory oscillations in the blood-filling of the extremities.

The first objection is done away with by the fact that in the case of preoccupation the fluctuations disappear (curve II) whereas the movements of the respiration-muscles continue. This phenomenon might likewise tell against the second objection, just as the fact that the subject always rested his hand on the bottom of the arm-baths. Hereby the movements of the upper-arm, which were already none too vigorous at first, were considerably relaxed if not checked entirely. However, with six subjects I have registered the movements of the upper-arm with the aid of a very sensitive tambour affixed to the arm-bath, its rubber membrane, which is provided with a knob, resting on the *m. biceps*. Hereby it was proved that the movements of the upper-arm do not affect the shape of the galvanogram. This is illustrated in Curve III where the movements of the upper-arm are reproduced graphically; of oscillations in the level of the galvanic curve, on the other hand, no trace is to be seen. Curve IV further shows that even considerably stronger involuntary arm-movements do not alter the shape of the galvanogram.

Finally, that the electric modifications in respiration cannot be ascribed to the bloodfilling of the extremities is demonstrated by curve V, which exhibits distinct respiratory oscillations of the galvanogram, although the extremities, from which current were derived, had been made bloodless by bandaging.

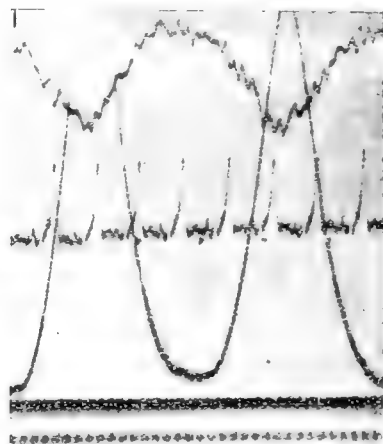


I. G. T. H. ♀ 22 years 3 VI '22. Lead I. Comp. Rest-curve.



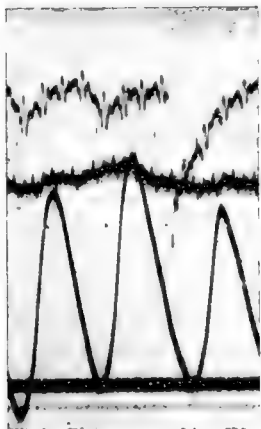
II. The same. 3 VI '22 Lead I. Comp. Pre-occupation curve.

Movement-curve;
 right upper-arm.

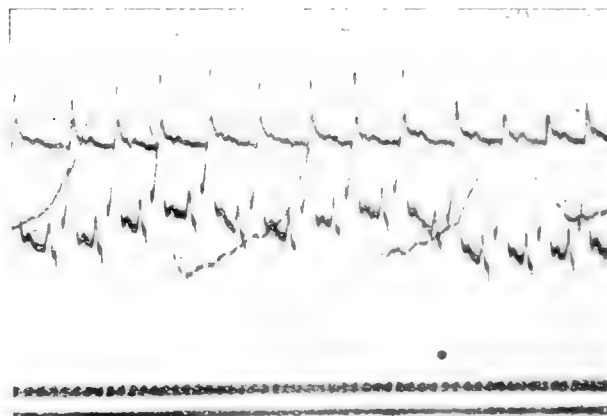


III. S. v. d. G. ♀ 31 years 19 VI '22. Lead II. Comp. Pre-occupation-curve, with control.

Movement-curve;
 left upper-arm



IV. G. T. ♀ 39 years 6 VI '22. Lead III. Comp. Rest-curve, with control.



V. D. T. ♂ 21 years 9 VI '22. Lead II. Comp. Rest-curve with dehematized right arm and left leg. Plethysmogram left hand.

SUMMARY.

The galvanogram of Man displays with a low degree of consciousness, oscillations which run parallel to respiration and are very likely connected with the respiratory oscillations in the condition of balance in the involuntary nervous system, as these oscillations disappear with preoccupation and as they are not influenced by the involuntary respiratory movements of the arms and are not the outcome of the modifications in the bloodfilling of the extremities, from which the current is derived.

June 1922.

*From the Laboratory for Psychiatry
of the Groningen University.*

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XXV

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Palaeontology and Zoölogy. — "*Phylogenetic and Ontogenetic Increase of the Volume of the Brain in Vertebrata*". By Prof. EUG. DUBOIS.

(Communicated at the meeting of June 24, 1922).

One of the most striking and important palaeontological facts ever brought to light in the investigation of the strata of the earth, is that of the extremely slight volume which the encephalon possesses in the earliest forms of Reptiles, Birds and Mammals. By this feature do these for the rest very differentiated and often gigantic earliest representatives of their class differ from the forms immediately following them and from the modern ones, in a way which must almost seem ridiculous to the comparative anatomist.

As regards Reptiles this has especially become known, by the discoveries of MARSH, about the Dinosauria, the principal terrestrial animals of the Mesozoic Era. In them the spinal canal, in its whole length, was not seldom wider than the cranial cavity. In *Stegosaurus*, from the Lowest Cretaceous in Wyoming, the cross-section of the sacral enlargement of the spinal canal (this in connection with the large hind-legs) was ten times as large as the cranial cavity. In a *Diplodocus* of a computed body length of 24 meters, from the same strata, this cavity is only 9 cm. long and 5 cm. wide, whereas that of an adult alligator, with a tenth of that maximum body length of its mesozoic distant relation, has a length of 6½ cm. and a width of 3 cm. Also in Theromorpha and Pterosauria the cranial cavity is very small.

Ichthyornis, described by MARSH from the Upper Cretaceous of Kansas, possessed only the third of the cranial capacity of the Large Sea Swallow (*Sterna cantiaca*), with which this toothed Mesozoic bird bore considerable resemblance in size and structure of its skeleton, probably also the mode of life of the two birds was similar.

In the class of the Mammalia, the Eocene primitive Carnivora, the *Creodontia*, possessed very little encephalon, which appears clearly on comparison of the cast of the brain-cavity of *Arctocyon*, from the Basal Eocene of Reims, with that of a dog of similar size of body (Fig. 1, A). The *Condylarthra* from the Lower Eocene, from which the existing sub-orders, the *Perissodactyla* and *Artiodactyla*

both originated, had also brains of incomparably small volume; side by side with the brain cast of *Phenacodus*, from the Wasatch Formation of Wyoming, that of a pig of similar size of the body appears as gigantic (Fig. 1, B). Also other Eocene Hoofed Mammalia, the *Amblypoda*, had very small brains. Thus *Coryphodon*, from the Wasatch Formation, in comparison with a *Rhinoceros* of similar size (Fig. 1, C).

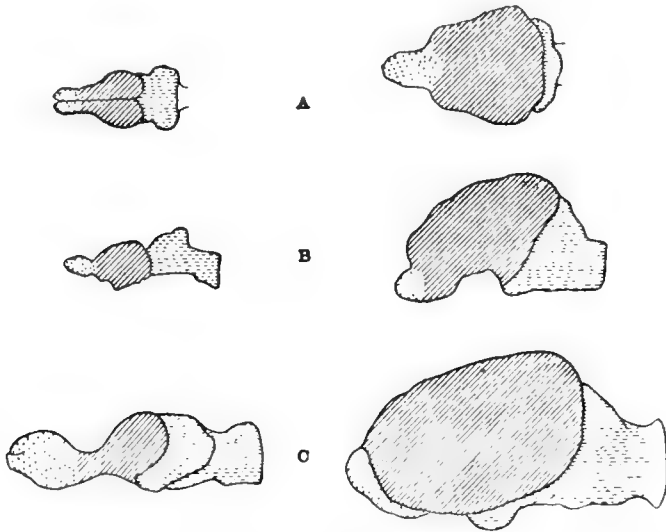


Fig. 1. Brain cast of: A. *Arctocyon* and *Canis*; B. *Phenacodus* and *Sus*; C. *Coryphodon* and *Rhinoceros*. (After OSBORN¹⁾).

In all these cases the most compounded, functionally most intricate parts of the encephalon, especially the cerebrum (hatched in Fig. 1), have the smallest volume. They in particular have not yet come to a fuller growth. But in the Miocene, partly already in the Eocene Period, the brain in the Mammalia reaches the volume and the proportion of its sub-divisions of most modern types.

As remarkable as this sudden, at all events comparatively rapid increase of the volume of the brain in the classes of Reptiles, Birds, and Mammals is the other paleontological fact, that in the Hominides, which geologically do not appear until very late, the brain immediately possessed the same volume already in the earliest of the known crania as in modern ones. The expectation that by means of these skulls a gradual increase of the volume of the brain might be shown, up to the exceptional capacity whose possession raises

¹⁾ H. F. OSBORN, *The Age of Mammals in Europe, Asia and North America*, p. 173. New York 1910.

modern Man so high above the animals, has not been realized. This however does not apply to Pithecanthropus, if this fossil anthropomorphous Primate is not considered to be of a separate family, but reckoned to belong to the Hominides. For he possessed only *two thirds* of the cerebral volume of the Australian aboriginal (which he resembled in body size and also in the main features of his skeleton), but *twice* that of anthropoid apes of the same body size. But also this "precursor of Man" is of a late date — probably not before the Pliocene. The transition from such a volume of brain as that of the Anthropoid Apes to the modern human volume seems at all events to have been a rapid one, and halfway there is still that of Pithecanthropus.

This organ, upon which depend inscrutable attributes of animal life, of the greatest degree, shows therefore an indubitable progress in the geological past. But it is also certain that this phylogenetic growth of the encephalon, as a whole and in its most compounded parts, took place with starts, and much seldomer than that of the other parts of the body, of which now one part, now another is again and again seen, in the most diversified ways, to increase in volume and complexity, the whole body not seldom growing into gigantic dimensions.

The question now suggests itself what the proportion has become between the volume of the brain and the size of the body through phylogenetic and ontogenetic growth, i. e. increase from species to species and from individual to individual, in adult animals of the present time.

It can easily be ascertained that the brain volume, reached by a species of animals in adult state, depends both on the size of the body and on the stage of development attained by the brain, which determines the degree of the functions of the organ.

It is not astonishing that the absolute brain weight of Man is surpassed by that of the Elephant and the large whale species. The largest whale species, which is a thousand times heavier than Man, possesses five times his brain weight. It is also self-evident that such a gigantic species of the cat family as the Tiger has much larger brain than the Domestic Cat; to sixty-four times the body weight of the latter, the Tiger has ten times its brain weight. Keeping to the same species we find in an adult dog of the size of the Wolf, of about 40 kg. body weight, double the brain weight of a lap-dog weighing about 2 kg.

But besides on the size of the body, the brain volume depends also on the stage of development of this organ, on the particular

structure and functions of other organs, and on other not easily measurable factors which determine the cephalisation of the central nervous system. When we compare Man with animals of the same body weight, when, in other words, we eliminate the factor body weight, we see that he far surpasses all the animals. He possesses three times the brain weight of a species of anthropoid apes of the same weight and more than six times that of an equally heavy gazelle. We may also say that the coefficient of cephalisation α of Man is three times as great as that of Anthropoid Apes and more than six times as great as that of the Gazelle.

We may assume equal cephalisation for the Cat and the Tiger, and yet we see the body weight increase in a much greater proportion than the brain weight. The same fact is found on comparison of the Mouse with the Rat, of the Pigmy Antilope with the Beisa-Antilope etc. Evidently the weights of brain and body, also with equal development of that organ, are not simply proportional to each other. The large species of the same genus, and also the large adult individual of the Domestic Dog species always has less brain weight in ratio to the body weight than the small species and the small adult individual. On account of the equality of the densities, the volumes may be substituted for the weights, and it is, therefore, possible that another measure of the body than the volume, for instance the surface, which is proportional to the $2/3$ power of the volume, — for which the weight P of the large animal may be put, and the weight p of the small one, — determines the quantity of brain — volume or weight — of the species. A priori it seems, indeed, that there is a good deal to be said for this view, for the sensual areas, the physiological cross-sections of the muscles, which determine muscular force, the superficial extent of the body, on which metabolism depends, are proportional to the surface of the body. The brain weights E and e of two animals differing only in body weight, but with for the rest quite identical organisation, may always be put $E = \alpha P^r$ and $e = \alpha p^r$; then the exponent of relation r , indicating the power of the body weight with which the brain weight increases or decreases, can be calculated from the equation $r = \frac{\log E - \log e}{\log P - \log p}$

and $\alpha = \frac{E}{P^r}$ will be found.

Twenty-five years ago, making use of the observations of weight published by MAX WEBER ¹⁾ a year before, I found thus $5/9$ as mean

¹⁾ MAX WEBER, Vorstudien über das Hirngewicht der Säugethiere, in Festschrift für CARL GEGENBAUR, p. 105–123. Leipzig 1896.

value of r in seven pair of mammalian species, i.e. a slightly smaller exponent than would correspond to the proportionality of the brain weight with the surface dimensions of the body ¹⁾. The discrepancy appeared to be constant, and the same exponent was found for Birds by LOUIS LAPICQUE and PIERRE GIRARD in 1905 ²⁾, and for Reptiles and Fishes by me in 1913 ³⁾. The exponent $\frac{5}{9}$ holds undoubtedly for all Vertebrata. Certainly this "strange power" of the body weight cannot be attributed to insufficiency of the data; it is impossible that we have to do here with a "rough empirical law, as limit of a sum of different functions". The relation found between the weights of the brain and the body must be a simple, rational one. As this exponent indicates the relation of species to species, a relation which must have come about with the origination of the species, I will designate it here as phylogenetic exponent.

In the system of coördinates of Fig. 2 the body weights in kg.

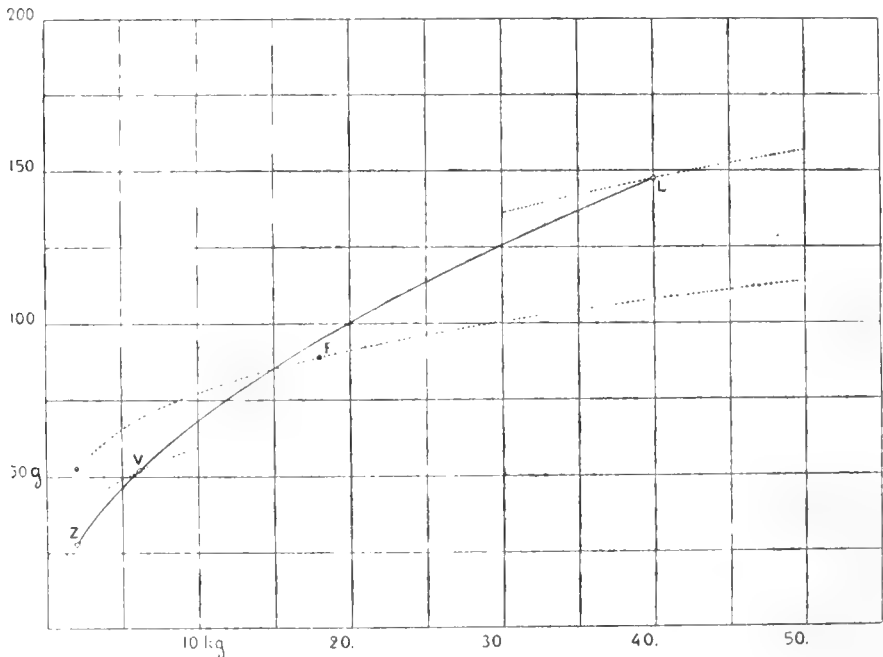


Fig. 2

¹⁾ Eug. Dubois, De verhouding van het gewicht der hersenen tot de grootte van het lichaam bij de Zoogdieren. Verhandelingen der Kon. Akademie van Wetenschappen te Amsterdam. Tweede Sectie. Deel V, N^o. 10. 1897. — Also: Sur le rapport du poids de l'encéphale avec la grandeur du corps chez les Mammifères, in Bulletins de la Société d'Anthropologie de Paris 1897, p. 337—376.

²⁾ Comptes Rendus des séances de l'Académie des Sciences. Paris 1905, 1, Tome 140, p. 1057—1059.

³⁾ These Proceedings, Vol XVI, p. 651—654. 1914.

are indicated on the abscissa, the brain weights in gr. on the ordinate. The points *Z*, *V*, *F*, and *L* refer to the averages of those weights of the species *Canis zerda*, *Canis vulpes*, *Canis familiaris* and *Canis lupus*. The relation of brain weight and body weight in these species of the genus *Canis* is here graphically represented by the full exponential curve *ZVL*, defined by the equation $E = 0.41 P^{5/8}$, and by the point *F*, whose position is defined by the equation $89 = 0.385 \times 18000^{5/8}$. In Fig. 3 the same relation is

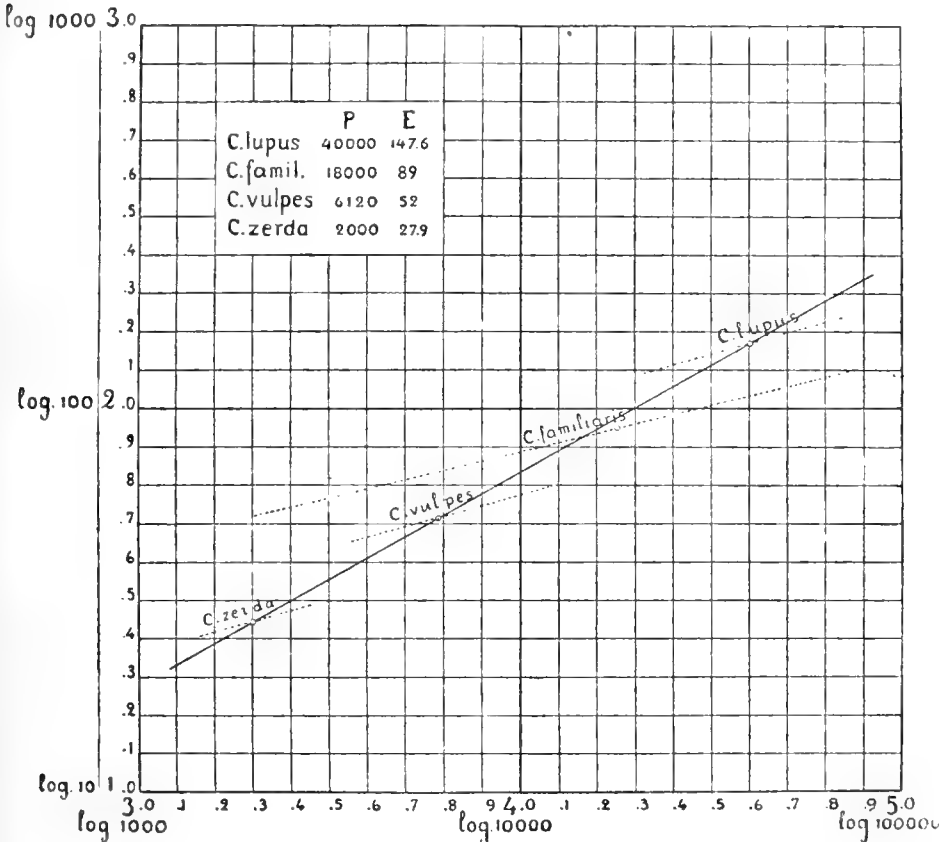


Fig. 3

represented by the full logarithmic line, a straight line with which the lines of genera and species with other cephalisation would run parallel.

An entirely different exponent of relation, viz. about $1/4$, i.e. less than $5/18$, half the value of the exponent holding from species to species, was found on comparison of large adult individuals of one and the same species by LAPICQUE for the Domestic Dog ¹⁾ in 1898,

¹⁾ L. LAPICQUE, Sur la relation du poids de l'encéphale au poids du corps. Comptes rendus de la Société de Biologie. Paris 1898, p. 63.

and independently of the distinguished French physiologist, in the same year, by me for Man¹⁾. In 1907 this result was confirmed by LAPICQUE²⁾ for Man; at present, from the new observations of weight on 150 Berlin dogs by BERTHOLD KLATT³⁾ I can corroborate the result obtained by LAPICQUE from RICHTER'S 188 Paris dogs⁴⁾.

Similar low interindividual exponents of relation as for Man and the Domestic Dog are now also valid within other species. For obvious reasons: very important differences of the body weights in one case, numerousness of the observations of weight in the other, the species Domestic Dog and Man are most suitable for a comparison of the individuals. But we so often meet with similar values, lying in the neighbourhood of $\frac{5}{18} = 0.27$ or lower, within other species, that here the existence of another, but equally real law may be admitted.

The same relation of brain weight and body weight as between large and small adult individuals of Man and the Dog is certainly also valid for the Horse. The data are not very numerous here, but the differences in body weight are comparatively large. A heavy Belgian horse, according to CORNEVIN⁵⁾, weighed 1040 kg. when alive, and its cranial capacity was 805 c.c.; a light Camargue horse had only 320 kg. living weight, and its cranial capacity was determined at 585 c.c. From this an exponent of relation of 0.2708 can be calculated. Prof. J. C. EWART at Edinburgh was so kind as to send me, for measurement, the skull of a very typical Shetland pony, a mare of $36\frac{1}{2}$, inches or $92\frac{1}{2}$, cm. height. Length of skull, from incisivi to occiput, $40\frac{1}{2}$, cm. The capacity is 475 c.c. I owe to Dr. C. KERBERT the communication of the body weight of such a pony living in the Amsterdam zoological gardens, a male

1) EUG. DUBOIS, Ueber die Abhängigkeit des Hirngewichtes von der Körpergrösse beim Menschen. Archiv für Anthropologie. Band 25, p. 423—441. Braunschweig. 1898.

2) L. LAPICQUE, Le poids encéphalique en fonction du poids corporel entre individus d'une même espèce. Bulletins et mémoires de la Société d'Anthropologie de Paris. Séance du 6 Juin 1907. 5^{me} Série, Tome 8, p. 315. Paris 1908.

3) BERTHOLD KLATT, Studien zum Domestikationsproblem: Untersuchungen am Hirn. Bibliotheca Genetica (E. BAUR). Band II. 180 pag. My calculations are to be published in Bijdragen tot de Dierkunde. XXII. Hat sich das Gehirn beim Haushunde, im Vergleich mit Wildhundarten, vergrössert, oder verkleinert? Leiden 1922.

4) CHARLES RICHTER, Poids du cerveau, de la rate et du foie, chez les Chiens de différentes tailles. Physiologie. Travaux du Laboratoire de M. CHARLES RICHTER. Tome Deuxième, p. 381—397.

5) CH. CORNEVIN, Examen comparé de la capacité crânienne dans les diverses races des espèces domestiques. Journal de médecine vétérinaire et de zootechnie, publié à l'École de Lyon, 3^{me} Série, Tome 14, p. 24. 1889.

horse of the same height (92 cm.) and skull length (41 cm.); it was 128 kg. By comparison with CORNEVIN's heavy Belgian horse I now find an exponent of relation of 0.2528. The heaviest of 15 male horses, according to COLIN¹⁾, a Percheron of 501 kg. dead weight, compared with the lightest male horse ("de petite taille") of this group, of 288 kg. dead weight, gives an exponent of relation of 0.1855. The heaviest horse was probably less emaciated than the lightest; hence the exceedingly low exponent.

For two groups, each of six domestic rabbits, formed from MÜLLER's records²⁾, one of an average body weight of 4386 gr., the other of 1727 gr., I find an exponent of relation of 0.2512. Two groups, each of five male moles, from MANOUVRIER³⁾, yield 0.234.

Eight domestic ducks, of 1756 gr. average body weight, compared with a dwarf of the same domestic species, of 755 gr. body weight, according to TIMMANN's⁴⁾ records, yield an exponent of relation of 0.3096. A cock of 1745.7 gr. body weight with a hen of 985.2 gr., from FALCK's⁵⁾ report, yield an exponent of relation of 0.2248.

Two groups, each of six Bull Frogs (*Rana catesbyana*), according to DONALDSON⁶⁾, of 244.5 and 164 gr. mean body weight, give an exponent of relation of 0.2516. Also the average cranial capacities of 9 male and 11 female Australian aborigines in relation to the mean volumes of the six long bones, from HAUGER's observations⁷⁾, yield an exponent of 0.2770.

In the Figures 2 and 3 the dotted lines give a graphical record of the relations of the weights of the brain and the body between

¹⁾ G. COLIN, *Traité de physiologie comparée des animaux*. 3^{me} Édition, Tome I, p. 302. Paris 1886.

²⁾ E. MÜLLER, *Vergleichende Untersuchungen an Haus- und Wildkaninchen*. *Zoologische Jahrbücher*. (Spengel). Abteilung für Allgem. Zoologie und Physiologie der Tiere. Band 36, p. 585. Gesamttabelle XXVa. Jena 1919.

³⁾ L. MANOUVRIER in *Dictionnaire de Physiologie* par CH. RICHEL, article „Cerveau”, p. 680. Paris 1898.

⁴⁾ O. TIMMANN, *Vergleichende Untersuchungen an Haus- und Wildenten*. *Zoologische Jahrbücher*, *ibid.*, p. 653.

⁵⁾ C. PH. FALCK, *Beiträge zur Kenntnis der Bildungs- und Wachstumsgeschichte der Thierkörper*. *Schriften der Gesellschaft zur Beförderung der gesammten Naturwissenschaften zu Marburg*. Band 8, p. 242. Marburg 1857.

⁶⁾ H. H. DONALDSON, *On a Formula for Determining the Weight of the Central Nervous System of the Frog from the Weight and Length of its Entire Body*. *University of Chicago Decennial Publications*. Vol. 10. (1902), p. 7.

⁷⁾ OTTO HAUGER, *Der Gehirnreichtum der Australier und anderer Hominiden, beurteilt nach ihrem Skelet*. *Anatomische Hefte (Merkel und Bonner)*. I. Abteilung. Heft 179. Band 59, p. 589: Tabelle I, p. 616—617: Tabelle III. München und Wiesbaden 1921.

adult individuals of four species of the genus *Canis*. In Fig. 2 they are again exponential curves, defined, for the Domestic Dog, by the equation $E = f P^{0.24} = 8.475 P^{0.24}$ (in which f is found from $89 = f \times 18000$), and for the wild Canidae, $E = 4.615 P^{5/18}$ (in which $4.615 = \frac{52}{6120^{5/18}}$). In Fig. 3 they are straight lines, both of them less steep than the lines for these relations from species to species, which they intersect in the points of the means, as far as the wild species are concerned. I have derived the mean point for the Domestic Dog, and the line for the individual relation within this species from observations of weight on 434 dogs, i. e. 152 new ones by KLATT ¹⁾, RICHTER'S 188 observations ²⁾, LAPICQUE and DHÉRÉ'S 47 ³⁾, RÜDINGER'S 19 ⁴⁾, WILDER'S 16 ⁵⁾, MAX WEBER'S 12 ⁶⁾. On the ground of these data 18 kg. may be admitted for the mean weight of the Domestic Dog, 89 gr. for its mean brain weight. The brain weight is certainly at least 6%, probably 10% lower than in a wild species of *Canis* of the same weight. This can only be considered as a consequence of domestication, i. e. of unnatural mode of living. Something of the same kind was found by DONALDSON and HATAI ⁷⁾ in the domesticated albino-form of the Brown Rat (*Mus norvegicus*). Not only the body weight has been reduced in this domestic Rat, but the brain weight comparatively to a greater degree, a phenomenon of domestication due to a diminished growth of the brain, which was already known to DARWIN (1868) for the domestic Rabbit ⁸⁾, and which was afterwards confirmed by LAPICQUE ⁹⁾, KLATT ¹⁰⁾, and

¹⁾ B. KLATT, l.c. Haupttabelle at the end of his work.

²⁾ CH. RICHTER, l.c.

³⁾ L. LAPICQUE in Bulletins et mémoires de la Société d'Anthropologie de Paris 1907, p. 316.

⁴⁾ N. RÜDINGER, Ueber die Hirne verschiedener Hunderassen. Verhandlungen der Anatomischen Gesellschaft. Jena 1894. Ergänzungsheft zum 9. Band (1894) des Anatomischen Anzeigers, p. 173—176.

⁵⁾ B. G. WILDER, Cerebral Variation in Domestic Dogs. Proceedings of the American Association for the Advancement of Science, 22nd Meeting (1873), p. 235—236. Salem 1874.

⁶⁾ MAX WEBER, Vorstudien über das Hirngewicht der Säugethiere l.c., p. 112.

⁷⁾ H. H. DONALDSON and SHINKISHI HATAI, A Comparison of the Norway Rat with the Albino Rat. Journal of Comparative Neurology. Vol. 21 (1911), p. 417—458, particularly p. 454—455.

⁸⁾ CH. DARWIN, The Variation of Animals and Plants under Domestication. Chap. IV.

⁹⁾ L. LAPICQUE in Bulletins et mémoires de la Société d'Anthropologie de Paris 1907, p. 331—337: „Régression cérébrale des animaux domestiques”.

¹⁰⁾ B. KLATT, Ueber die Veränderung der Schädelkapazität in der Domestikation. Sitzungsberichte der Gesellschaft Naturforschender Freunde zu Berlin. 1912, p. 155

MÜLLER¹⁾. The same cerebral regression by domestication was found by LAPICQUE²⁾ for the Ox and the Sheep, by KLATT³⁾ and BETHCKE⁴⁾ for the Ferret, by LAPICQUE⁵⁾ and TIMMANN⁶⁾ for the domestic Duck, and now by me for the Domestic Dog. For 72 of DONALDSON and HATAI's wild *Mus norvegicus*⁷⁾ of both sexes, of 335 to 525 gr., averagely 389.861 gr. body weight, with averagely 2.402 gr. brain weight, and 71 male and female wild rats of 275 to 325 gr., averagely 300.211 gr. body weight, with an average brain weight of 2.299 gr., I calculate an exponent of relation of 0.1674. That this exponent is considerably smaller than is usually found between individuals of one species, may be readily explained in this way that DONALDSON and HATAI give the body weights irrespective of the state of adolescence and the fat percentage (of which they state that it augments with age); part of the increase of the body weight is, therefore, not accompanied by increase of the brain weight, as is the case on comparison of adult individuals only, and which are in a medium condition.

In Fig. 4, after DONALDSON⁷⁾ the exponent of the individuals with body weights between 250 and 446 gr. may be calculated at 0.1572 for the male wild *Mus norvegicus* (from observations of weights on 232 male specimens of all ages). From DONALDSON's Table 85⁸⁾ the exponent 0.1554 may be calculated for body weight of 301.0 to 389.7 gr. The exponent is 0.1342 for the male albino of this species of 181 to 350 gr. body weight. The relatively smaller increase of the brain weight with increasing body weight of the (domestic) albino Rat finds expression in the slower ascent of the curve and the lower value of the exponent. It may be admitted that the exponent is in general somewhat lower in the domesticated species (not leading a natural life), because the brain increases somewhat

¹⁾ E. MÜLLER, Vergleichende Untersuchungen an Haus- und Wildkaninchen. Loc. cit. p. 503—588.

²⁾ See note 9 foregoing page.

³⁾ See note 10 foregoing page.

⁴⁾ H. BETHCKE, Vergleichende Untersuchungen an Frettchen und Iltissen. Ibid., p. 589—620.

⁵⁾ O. TIMMANN, Vergleichende Untersuchungen an Haus- und Wildenten. Ibid., p. 621—656.

⁶⁾ DONALDSON and HATAI, l.c., p. 426—427.

⁷⁾ From Chart 31, p. 201 in H. H. DONALDSON, The Rat. Reference Tables and-Data for the Albino Rat (*Mus norvegicus albinus*) and the Norway Rat (*Mus norvegicus*). Memoirs of the Wistar Institute of Anatomy and Biology. N^o. 6. Philadelphia 1915.

⁸⁾ Ibid, p. 208.

less under these circumstances, in proportion to the body weight grows in a less degree than in the natural state.

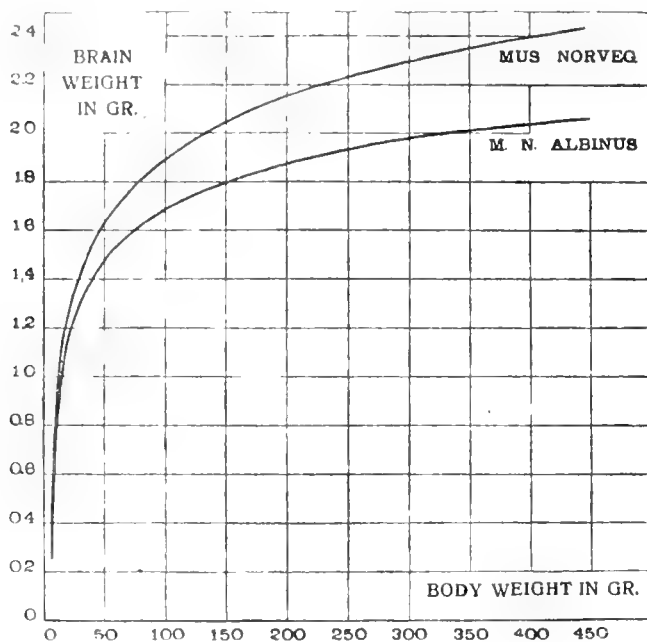


Fig. 4.

In 1918 I found an exponent of $5/18 = 0,27$, i.e. of precisely half the value of the exponent holding for the relative brain weights from species to species, on comparison of the volumes of largest, i.e. of full-grown, homologous nerve or ganglion cells in relation to the body weights of adult animals of very different sizes, both of one species and of different species. Compare Tables I and II¹⁾).

Though in the microscopical image of the grey cortex the nerve cells are placed as densely and are as unequal in size as the stars in the telescopic image of the Milky Way, we may yet admit a relation between the average size of these cells and the size of the body, and look for the explanation of the relation holding for the volume of the brain in the nerve cells, the elements from which the brain is composed.

The exponent holding between the adult individuals of one and the same species, in the relation of the body weight to the brain weight, may now be distinguished as ontogenetic exponent from

¹⁾ These Proceedings, Vol. XX, p. 1328—1334. There too the fuller references to the works of the authors mentioned in the last column of Table I.

T A B L E I

| | Body weight (grammes) | Nerve cell | | Reference to authors, date and page of reported measurements |
|--------------------------------------|-----------------------|-----------------------|--------------|--|
| | | Mean diameter (Micra) | Des-cription | |
| 1. <i>Elephas indicus</i> | 3600000 | 84.4 | Col. ant. | I. Hardesty. (1902). 160, 161 |
| 2. <i>Equus caballus</i> | 562500 | 61.9 | " " | " " " " " |
| 3. <i>Homo sapiens</i> | 72000 | 58.0 | " " | " " " 159, 160 |
| 4. <i>Lepus cuniculus dom. A.</i> | 2000 | 39.2 | " " | " " " 160 |
| 5. <i>Mus norvegicus albinus. A</i> | 250 | 34.7 | " " | " " " " |
| 6. <i>Mus musculus albinus</i> | 20 | 27.4 | " " | " " " 160, 164 |
| 7. <i>Lepus cuniculus dom. B</i> | 2000 | 56.0 | Spin. | G. Levi. (1908). 200 |
| 8. <i>Mus musculus. A</i> | 20 | 37.2 | " | " " " " " |
| 9. <i>Canis familiaris. A</i> | 23000 | 80.8 | " | " " (1906). 331, 332 |
| 10. <i>Canis familiaris. B</i> | 3750 | 67.5 | " | " " " " " |
| 11. <i>Mus norvegicus albinus. B</i> | 250 | 16.5 | Purk. | Addison. (1911). 469 |
| 12. <i>Mus musculus. B</i> | 20 | 13.0 | " | Obersteiner. (1913). 5 |
| 13. <i>Felis leo</i> | 119500 | 69.5 max. | Betz | Brodmann. (1909). 83 |
| 14. <i>Felis pardalis</i> | 10433 | 66.5 med. | " | Bevan Lewis. (1880). 53 |
| 15. <i>Felis domestica</i> | 3300 | 69.0 max. | " | Brodman (Lewis) (1909). 83 |
| | | 60.0 med. | " | Bevan Lewis. (1880). 85 |

the exponent holding from species to species, as it expresses the relative individual growth of the brain to the adult state.

In consequence of this difference in the fixed relations of the weights of the brain and the body, between homoneuric species on one side, individuals of a species on the other side, i. e. the difference between the phylogenetic and the ontogenetic exponent, small individuals have comparatively more, large individuals comparatively less brain than species of corresponding mean body weight.

This appears graphically in Figures 2 and 3. The difference can become very great in dwarfs and giants of one species; it is very striking in the Figures 5 and 6, which give the accurate outlines, in natural size, of the skull of a medium sized fennec (*Canis zerda*), the smallest species of the genus *Canis*, and one of the smallest individuals of the species Domestic Dog, of a diminutive breed,

TABLE II

Calculated Values of the Exponent r for the Increase of the Volume
of the Nerve Cells with the Body Weight

| | Nerve cell Description | Proportion of the body weight | Exponent |
|---|---------------------------|-------------------------------------|----------|
| 1. <i>Elephas indicus</i> and <i>Mus musculus albinus</i> | Col. ant. | 180000 : 1 | 0.2789 |
| 2. <i>Equus caballus</i> and <i>Mus musculus albinus</i> | " " | 28125 : 1 | 0.2387 |
| 3. <i>Homo sapiens</i> and <i>Mus musculus albinus</i> | " " | 3600 : 1 | 0.2747 |
| 4. <i>Lepus cuniculus dom. A</i> and <i>Mus musculus albinus</i> | " " | 100 : 1 | 0.2333 |
| 5. <i>Mus norvegicus albinus. A</i> and <i>Mus musculus albinus</i> | " " | 12.5 : 1 | 0.2805 |
| 6. <i>Lepus cuniculus dom. B</i> and <i>Mus musculus. A</i> | Spin. | 100 : 1 | 0.2665 |
| 7. <i>Canis familiaris. A</i> and <i>Canis familiaris. B</i> | " | 6 : 1 | 0.2975 |
| 8. <i>Mus norvegicus albinus. B</i> and <i>Mus musculus. B</i> | Purk. | 12.5 : 1 | 0.2832 |
| 9. <i>Felis leo</i> and <i>Felis domestica</i> | Betz | 36 : 1 | 0.2804 |
| 10. <i>Felis pardalis</i> and <i>Felis domestica</i> | " | 3 : 1 | 0.2681 |

probably a toy-terrier, of the same body weight, after photographs which I owe to Prof. W. LECHE at Stockholm. The brain weight in the diminutive individual of Domestic Dog, with only a ninth of the mean body weight of the species, is indeed quite 87% more than the mean of the smallest species of *Canidae*¹⁾. The amount and the plus or minus sense of this difference with species is dependent on their body weight. The smaller the species of the genus *Canis*, the more it is exceeded in brain weight by an individual of the same size of the Domestic Dog species. Domestic dogs of the size (the body weight) of the common (Euro-

¹⁾ The body weight of a female fennec, killed in its African home, was 1.5 kg. according to KLATT (Studien zum Domestikationsproblem, p. 36), the weight of the brain was 25.2 g. The capacity of an almost adult female skull in the Leiden Museum of Natural History, observed by me, was 20 c.c., of two other skulls, of which the sex is not indicated, in the Berlin Zoological Museum, the capacity observed by KLATT, is resp. 20 and 18 c.c. When for the species 2 kg. body weight, and 27.9 gr. brain weight is assumed, this gives certainly about the true ratio; absolutely these weights are possibly estimated too high. From the observations of KLATT (ibid., Haupttabelle) on 17 adult toy-terriers (*Zwergpinscher*), of an average body weight of 3.11 kg., with 58.1 gr. brain weight, I calculate for 2 kg. body weight of this diminutive breed the brain weight at 52.3 gr.

pean) Fox have only slightly more than **28** % more brain weight than this small species. Very large domestic dogs, of about 40 kg.,

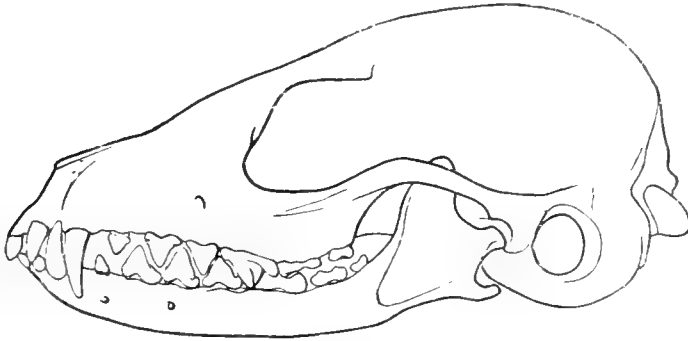


Fig. 5.
Skull of a fennec (*Canis zerda*), in natural size.

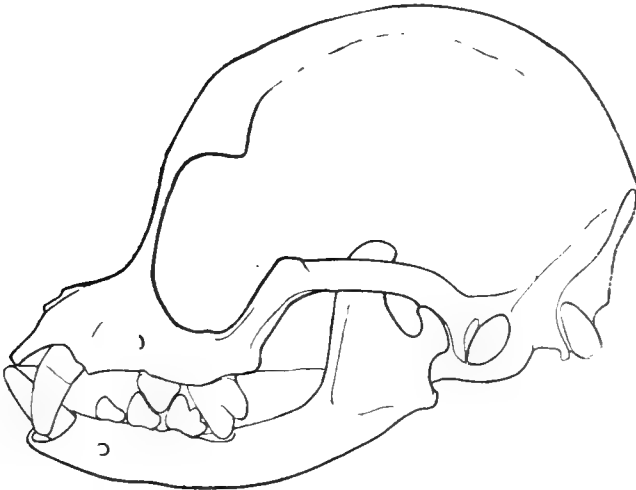


Fig. 6. Skull of a domestic dog of diminutive breed, in natural size.

i.e. the mean body weight of the Wolf, have **25** % less brain weight than this largest member of the Canidae¹⁾.

It is now of great importance that the ontogenetic exponent is equal to the exponent indicating the relation of the body weights or

¹⁾ Through comparison with two foxes from France and one wolf from America LAPICQUE (loc.cit. p. 329) had already pointed out these differences in 1907. Afterwards KLATT (ibid., p. 36) corroborated them with more numerous data through a comparison with the Jackal and the Wolf. According to KLATT'S records on ten (German) foxes (ibid., p. 37) and eleven domestic dogs (Haupt-tabelle) of about the same size, 6.12 kg. may be taken for the body weight of

volumes to the volumes of homologous nerve or ganglion cells, both between adult individuals of one species and between different species. This confirms that, with increasing body weight, from adult individual to adult individual of one and the same species, only the volume of each nerve cell in the brain increases, but from species to species at the same time the number of these cells, and that the number does so in the same ratio as the volume increases, which had already been rendered probable by other facts. Comparison of the brain weight in function of the body weight between the two sexes¹⁾ had led me to the result, on the ground of the measurements of the diameter of the muscle fibres by BOWMAN and by SCHWALBE and MAYEDA, and the observations of muscle weights by THEILE, that the number of muscle fibres of Man is equal to that of Woman. From the comparison of the relative quantity of brain and muscularity of the Europeans and the Japanese it had appeared to me that the relatively larger volume of the brain and of the muscles of the latter finds its explanation, not in the different number of the neurones and the muscle fibres, but in the larger cross-section of the separate muscle fibres, larger separate volume of the nerve cells²⁾. Hence, between Man and Woman, between the Japanese and the European, i. e. within the species of *Homo sapiens*, only the volume, not the number of the nerve cells and of the muscle fibres differ.

the Fox, 52 gr. for its brain weight; the average body weight of the eleven domestic dogs is 6.6 kg., their average brain weight 68 gr. Hence with equal body weight, the latter brain weight is 28.4% more than for the Fox. Comparison of these dogs with the jackals (*Canis aureus*) leads to similar results. The average body weight of fourteen jackals according to KLATT's observations (Haupt-tabelle) is 6.836 kg., their average brain weight 57.1 gr. The difference with dogs of the same body weight is 20.1%, somewhat less than the difference of these with the Fox, because the cephalisation of the Jackal is a little higher. In contrast with domestic dogs of the size of these small Canidae, domestic dogs of the size of the Wolf have 24.8% less brain than averagely this largest species of the genus *Canis*. From KLATT's records (Haupt-tabelle) of brain weights of six and body weights of four Lapland and Russian wolves, and of cranial capacities of 23 European and American wolves (KLATT, Ueber die Veränderung der Schädelkapazität, p. 166). averagely 161 c.c., I derived a body weight of the species of 40 kg., a brain weight of 147.6 gr. Absolutely both weights may be a little too high, relatively most likely they are about right. Accordingly the Wolf is about equal in its cephalisation with the Fox. But twenty dogs of KLATT's observations, of 30 to 48 kg., averagely 37.6 kg. body weight, have an average brain weight of 109.4 gr.

¹⁾ Under this title in these Proceedings, Vol. XXI, p. 868—869. (1919).

²⁾ Egg. Dubois, On the Significance of the Large Cranial Capacity of *Homo neandertalensis*. These Proceedings, Vol. XXIII, p. 1281. (1921).

From the still little known, but very important measurements of muscle fibres by VON DER MALSBURG¹⁾ the same may be derived for individuals of unequal size of different Mammalia.

In Table III some individuals of five species, being in a fairly good condition, and of a body weight as different as possible, are compared as regards the relation between the latter and the cross-section of homologous muscle fibres. This cross-section appears to increase in direct ratio to the surface of the body, hence to the cross-section of homologous muscles, which means that the number of muscle fibres within a species does not change with increasing size of the body. Also the number of nerve fibres and that of the nerve cells of the brain may then be admitted as being the same within a species.

This is certainly not the case between different species, for when the specific differences of caliber are taken into account, through which homologous muscle fibres of different species of animals (just as not homologous muscles of the same species) are distinguished, not much remains of a direct influence of the size of the body on this caliber of the muscle fibre. The number of the muscle fibres must, therefore, greatly increase with the size of the animal species. According to VON DER MALSBURG the average diameter of the muscle fibres in the rectus abdominis and the gastrocnemius is for the Ox 45.88 micra (in its different breeds 35.35 to 63.37 micra), for the Horse 39.20 micra (breeds 33.26 to 48.60 micra), for the Pig 42 micra, for the Sheep 22.61 micra (breeds from 18.50 to 30.85 micra), for the Goat 18.90 micra. For the average diameter of the muscle fibres in the gastrocnemius of the Dog (calculated from v. d. M.'s records, applied to the mean body weight of this species) 21 micra may be assumed, the average of four hares is 19.20 micra, and of five mice 17.40 micra, the body weights of these two last species being to each other as 200:1.

With not inconsiderable specific differences (but much smaller than between the different breeds and individuals), only small differences between these species are to be ascribed to the influence of the size of the body. Thus also MAYEDA and SCHWALBE²⁾ found in

¹⁾ KAROL VON DER MALSBURG, Die Zellengrösse als Form- und Leistungsfaktor der landwirtschaftlichen Nutztiere. Arbeiten der Deutschen Gesellschaft für Züchtungskunde. Heft 10. 367 pag. Hannover 1911.

²⁾ R. MAYEDA, Ueber die Kaliberverhältnisse der quergestreiften Muskelfasern. Zeitschrift für Biologie. (KÜHNE und VOIT). N.F. Bd. 9, der ganzen Serie Bd. 27, p. 129. München und Leipzig 1890. — G. SCHWALBE und R. MAYEDA, Ueber die Kaliberverhältnisse der quergestreiften Muskelfasern des Menschen. *Ibid.* p. 487, 489, 515.

TABLE III

Relation of the Cross-Section of Homologous Muscle Fibres to the Body Weight, in Individuals of Different Sizes of one Species

| Page with V. D. MALSBERG | Species | P Body weight, in kg. | ^m Diameter of the muscle fibres, in micra | | Calculated power of P, which is propor- tional to m^2 |
|-----------------------------|--|--------------------------------|--|---|---|
| | | | Gastro- cnemius | Mean of Rectus abdominis and Gastro- cnemius | |
| | Horse | | | | |
| 146 | 4 heavy, average | 712.5 | | 46.16 | 0.6459 |
| 146 | 2 light " | 290 | | 34.53 | |
| 102 | Belgian male | 850 | | 49.60 | 0.6750 |
| 102 | Pony, male | 300 | | 34.90 | |
| 102 | 5 males, average | 740 | 48.79 | | 0.7218 |
| 104 | 4 " " | 437.5 | 40.36 | | |
| | Ox | | | | |
| 95 | 4 bulls, average | 662.5 | 45.17 | | 0.6670 |
| 97 | 3 " " | 416.6 | 38.70 | | |
| 95 | Bos taur. primig. var. Sarm. | 600 | 45.00 | | 0.6030 |
| 98 | " " " " " | 350 | 38.25 | | |
| | Pig | | | | |
| 108 | Wild, male | 130 | 48.25 | | 0.7800 |
| 108 | " female | 80 | 40.10 | | |
| 149 | Yorkshire | 100 | | 44.00 | 0.5480 |
| 149 | " dwarf (^{much} emaciated) | 11.8 | | 24.50 | |
| | Dog | | | | |
| 109 | Newfoundland (emaciated) | 49 | 38.10 | | 0.7402 |
| 109 | Fox-Terrier | 9 | 20.35 | | |
| | Rabbit | | | | |
| 326 | Domestic, large breeds, average | 3.3 | | 36.65 | 0.6946 |
| 326 | " small " " | 1.5 | | 27.87 | |
| | | | | Mean | 0.6751 |

their measurements the muscle fibres in the gastrocnemius of a mouse about as thick as in the homologous muscle of a woman and of a dog (but thinner than in that of a man). In the masseter of their mouse the muscle fibres were about as thick as in the masseter of the man, but less thick than in the dog. That the size of the body from species to species has only little influence on the caliber of the muscle fibres appears also from this that G. LEVI¹⁾ found the diameter of the thickest muscle fibres in the rectus femoris of a mouse not below that in a rat (twenty times as heavy).

It may, therefore, be admitted that in homoneuric species the number of muscle fibres, and then also proportionally that of the ganglion cells in the brain, greatly increases with the size of the body. But the available data do not enable us to calculate the exact relation of the body weight to the number of the muscle fibres in these species. On the ground, however, on one side of the relation found for the brain weight E to the body weight P , according to which E increases proportionally to $P^{5/8}$ between homoneuric species, and proportionally to $P^{5/18}$ between adult individuals of the same species, and on the other side, on the ground of the relation found for the volume of the separate nerve cells C to the body weight, according to which C increases in the ratio of $P^{5/18}$, both between individuals and between species; further on the ground of the established fact that between large and small individuals the number of the muscle fibres, hence proportionally that of the nerve cells in the brain, does not differ, but that it differs greatly between large and small species, we may conclude, that also the number of the nerve cells between homoneuric species increases in the ratio of $P^{5/18}$.

The difference between the phylogenetic and the ontogenetic exponent is thus rationally explained. It means that in the origination of the species, increase of the size of the body is accompanied with multiplication of the nerve cells, through cell division (in non-homoneuric species this multiplication is greater in certain parts of the brain)²⁾. With the establishment of larger adult individuals

¹⁾ GIUSEPPE LEVI, Studi sulla grandezza delle cellule. Archivio di Anatomia e di Embriologia. Vol. V, p. 327. Firenze 1906.

²⁾ Direct counting of the cells in the grey cortex of Monkeys by OTTO MAYER (Mikrometrische Untersuchungen über die Zelldichtigkeit der Grosshirnrinde bei den Affen, Journal für Psychologie und Neurologie, Bd. 19, p. 237. Leipzig 1912) teaches that per m.m.², calculated throughout the cortex, only about the same number of cells occur in the small Hapale (3448) as in the larger Chrysothrix (3603) and in the still larger Cebus (3581). As the brain weights in these heteroneuric and from the smallest to the largest species higher cephalized American

of a species, there is no nerve cell division; these cells only increase in volume, which they also do with the origination of larger species. For this increase of the nerve cell volume is a mechanical necessity, as may appear further below.

That phylogenetic increase of the volume of the brain is actually brought about by cell division, associated with equivalent increase of the separate cell volume, is also proved by the fact that in related, but heteroneuric species, with equal body weight, the volumes (or weights) of the brain or — what comes to the same — with unequal body weight, the calculated coefficients of cephalisation, in many cases, are to each other as 1, 2, 3, 4. The cranial capacities of the Chimpanzee (450 c.c.), of *Pithecanthropus* (900 c.c.), and of the male Australian aboriginal (1350 c.c.) are to each other as the numbers 1 : 2 : 3. The coefficient of cephalisation of the Man-like Apes is twice that of the Old World Monkeys and Baboons; *Cebus* has double the cephalisation coefficient of *Chrysothrix*; in the Megachiroptera it is twice that of the Microchiroptera. The coefficient of the Tree Shrew (*Tupaja*) is four times that of the Common Shrew (*Sorex*) and the Musk Shrew (*Crocidura*). The coefficients of the genera *Mus*, *Lepus*, and *Sciurus* are to each other as 1 : 2 : 3. The genera *Tapir*, *Sus*, and *Hippopotamus* have a coefficient of cephalisation half as great as that of the Horses, the Deer, the Giraffe, the Antilopes, and the Oxen. The Chevrotain (*Tragulus*) also has a coefficient only half so great as the modern-type Ruminants. It is extremely interesting that among the Mustelidae, the Polecat (*Putorius putorius*), the Stoat (*Putorius ermineus*), and the Weasel (*Putorius nivalis*) possess a coefficient of cephalisation only half so great as the Beech-Marten (*Mustela foina*) and the Pine-Marten (*Mustela martes*). In this respect the Badger (*Moles*) agrees with the former, the Otter (*Lutra*) with the latter group.

We meet here with an important phenomenon, analogous to the "parameter-law" of crystals, and, undoubtedly, intimately connected with the polyploidy of nuclei and consequent rational increase of cell volume.

It may, further, be pointed out that most of the heteroneuric species mentioned with low cephalisation, are small, in comparison with the allied species with high cephalisation. This proves that the phylogenetic growth of the brain, in which — different from what

Monkeys are to each other as 8 : 24 : 70, the absolute number of cells increases considerably more than would correspond with the same size of body of homoneuric species. In the nearly homoneuric Gibbon (*Siamang*) and Chimpanzee those numbers are 3160 and 1765, and the brain weights to each other as about 1 : 3.

is found in the establishment of a new homoneuric species — certain parts of this organ increase to a greater degree than the other parts, and accordingly a heteroneuric species originates, is probably always too accompanied with increase of the bulk of the body. Only with the same increase of the bulk of the body, the increase of the volume of the brain is comparatively greater than in the establishment of a new homoneuric species.

Another peculiarity of the Polecat may be considered in connection with what has been said about its lower cephalisation. When with the observations of weight of the body and the brain by BETHCKE¹⁾ of ten certainly adult polecats, the ontogenetic exponent is calculated, from the five with body weights above 1000 gr. (average 1281.5 gr.) and the five under 1000 gr. (average 769 gr.), **0.42** is found for it, the same value as is obtained from the weights of a very large polecat (of 1700 gr.), from the observations of LAPICQUE²⁾, and a very small one (of 593 gr.), of my own observations³⁾, both adult animals. This exponent is exactly halfway between $\frac{5}{18}$ and $\frac{5}{9}$. In a graph the direction of the ontogenetic line of the Polecat would be seen to deviate from other ontogenetic lines, and approach to coincidence with the phylogenetic line of the genus *Putorius*. Evidently the species of Polecat is in a state of disintegration. Probably the other *Putorius* species are too. Well-known is, indeed, the great variability of all the species of this genus.

In the ontogenetic growth there is an important difference between the nerve cells and the other cells of the body. It is the great merit of GIUSEPPE LEVI and of EDWIN CONKLIN to have pointed this out. In 1906 LEVI⁴⁾ proved for a great number of Mammalia and in 1908 for the Vertebrates in general⁵⁾, that in contrast with most cells, except probably the muscle fibres (and those of the crystalline lens), the size of the nerve cell increases with the size of the animal⁶⁾. The other cells increase in number, not separately in size.

¹⁾ Loc. cit., p. 613.

²⁾ Comptes rendus. Académie des Sciences. (2), Tome 151, p. 1393. Paris 1912.

³⁾ Verhandeling of 1897, p. 36. Also: Bulletins de la Société d'Anthropologie de Paris, 1897, p. 371.

⁴⁾ Loc. cit.

⁵⁾ GIUSEPPE LEVI, I Gangli cerebrospinali. Supplementa al Vol. VII dell' "Archivio Italiano di Anatomia e di Embriologia". Firenze 1908.

⁶⁾ IRVING HARDESTY, already in 1902, found that the size of the motor nerve cells from the spinal chord of various Mammals increases with the size of the body. (Observations on the Medulla spinalis of the Elephant with some Comparative Studies of the Intumescencia Cervicalis and the Neurones of the Columna Anterior. Journal of Comparative Neurology. Vol. XII, p. 125 seq. Philadelphia 1902).

In 1912 CONKLIN¹⁾ showed for different species and individuals of one species of Boat Shell (*Crepidula*), that in spite of the very great differences in body size, "the size of tissue cells is approximately the same in all species examined, and in all individuals of both sexes and of very different sizes. In the main, differences in body size are due to differences in the number of cells present, and not to variations in the size of individual cells. Ganglion cells and muscle cells form the principal exception to this rule". (According to his measurements the diameter of muscle fibres is not greater in the larger species, and only a little greater in large-sized individuals of one species). From his measurements of a gigantic female and a medium-sized male individual of *Crepidula plana* I find for the exponent of relation of the volume of the body and the volume of the ganglion cells the value of 0.3149, which is sufficiently near $\frac{5}{18}$ to prove the existence of the same ontogenetic relation also in the Invertebrates.

As was already mentioned, LEVI is less certain in his conclusion about the muscle fibres; he generally finds them thicker in large animals than in small ones, but the thickness changes much less than the length, and there are many exceptions to the rule. This uncertainty is, indeed, explicable by what was derived above from VON DER MAJSBURG's measurements with regard to the larger differences between individuals than between the species.

The nerve cells and the muscle cells are distinguished from most other cells (only the fibres of the crystalline lens make an exception to the general rule) in that early in life — in Man and all Mammalia examined on this point about birth-time — they cease increasing in number through division, but then continue for some time to increase separately in volume. The other cells go on multiplying by division throughout life. The muscle cells continue increasing their separate volume at least up to the adult state of the individual. But the nerve cells also stop doing this in the early youth of the individual.

A consequence of this peculiarity of the nerve cells is, that early in the life of the individual the brain assumes the volume of the adult state of the body; in a male child for instance, at the age of nine, in a female child when six years old. But a similar remark holds among others for the Dog, the Rat, the Great Ant-Eater, the Sparrow, the Chicken, the Crocodile, the Frog, the Salmon,

¹⁾ EDWIN G. CONKLIN, Body Size and Cell Size. *Journal of Morphology*. Vol. 23, p. 159—188. Philadelphia 1912.

in short for all the Vertebrata, and also for the Invertebrata. At birth the brain weight of Man is $\frac{1}{9}$, and in the adult state of the body $\frac{1}{47}$ of the body weight. At its birth a dachshund has $\frac{1}{29}$, and in the adult state $\frac{1}{135}$ of its weight in brains. With a body weight of 7 grams the Brown Rat has less than $\frac{1}{10}$, and when it is full grown $\frac{1}{160}$ of its weight in brains. In the Bull Frog of $4\frac{1}{2}$ grams of body weight, the brain weight constitutes $\frac{1}{100}$ of it, and when the body weight has increased to 200 grams, the ratio of the brain weight is only $\frac{1}{1000}$. This gives the skulls, of them all in their first youth, a much more humanlike appearance than they have in the adult state. The great resemblance of the skull of young Apes with that of Man cannot, therefore, have the special significance that is sometimes ascribed to it.

The peculiarity of the nerve cells manifested in this early cessation of cell division in the ontogenetic growth, now accounts also for the long interruptions in the phylogenetic growth, (also resting on cell division), especially if this growth is stronger in certain parts of the brain and mostly in those with the highest integrative action. This phylogenetic growth then takes place with long intervals, as shown anatomically in the brain quantities of allied heteroneuric species of the present animal world, paleontologically by comparison of animal forms of the present time with those of a former world order.

But why are the nerve cells distinguished in this conspicuous way from all other cells, with the exception of the muscle cells, which act under their influence? We find the volume of the nerve cells to be in a particular, in what precedes not yet causally explained relation to the body weight. What is the meaning of that "strange" $\frac{5}{18}$ power? To a proportionality with the $\frac{6}{18}$ or $\frac{1}{3}$ power of the body weight, i.e. with the linear dimension of the body, we could readily ascribe a dynamic significance; as the mass of the body increases as P , the physiological cross-sections of the muscles, which determine the muscular force, the sensual areas, the areas that determine metabolism increase only proportional to $P^{\frac{2}{3}}$, it would be comprehensible if this inadequacy implied an increase of the volume of the nerve cell proportional to $P^{\frac{1}{3}}$. But this takes place in a definite, smaller proportion, according to $P^{\frac{5}{18}}$.

In order to detect the meaning of this latter proportionality I examined on a former occasion¹⁾ in what relation the volumes of the principal constituents of the nerve cell, the nucleus and the plasma, are to each other and to the body weight. The result of this examination is recorded in Table IV.

¹⁾ These Proceedings, Vol. XXII, p. 671—675. (1920).

TABLE IV

Calculated values of the exponents d , λ ($= 5/18 d$) and k for the increase of the plasma volume D with the cell volume C and with the body weight P , and of the nucleus volume K with the cell volume C . (From measurements of the diameters of ganglion cells and their nuclei by GIUSEPPE LEVI, and corresponding linear dimensions of their plasma).¹⁾

| Species | Situation of the ganglion cells | d in $\left(\frac{C}{C_1}\right)^d = \frac{D}{D_1}$ | λ in $\left(\frac{P}{P_1}\right)^\lambda = \frac{D}{D_1}$ | k in $\left(\frac{C}{C_1}\right)^k = \frac{K}{K_1}$ |
|--|---------------------------------|---|---|---|
| 1. <i>Bos taurus</i> , 1 and <i>Mus musculus</i> , 8 | Gangl. spin. | 1.198 | 0.3327 | 0.5348 |
| 2. <i>Bos taurus</i> , 2 and <i>Mus musculus</i> , 8 | id. id. | 1.203 | 0.3342 | 0.5268 |
| 3. <i>Lepus cuniculus</i> , 4 and <i>Mus norvegicus</i> , 7 | id. id. | 1.202 | 0.3338 | 0.5987 |
| 4. <i>Lepus cuniculus</i> , 4 and <i>Mus musculus</i> , 8 | id. id. | 1.206 | 0.3351 | 0.6143 |
| 5. <i>Mus norvegicus</i> , 7 and <i>Mus musculus</i> , 8 | id. id. | 1.210 | 0.3362 | 0.6288 |
| 6. <i>Cavia cobaia</i> , 5 and <i>Arvicola arvalis</i> , 9 | id. id. | 1.216 | 0.3378 | 0.6703 |
| 7. <i>Cavia cobaia</i> , 6 and <i>Arvicola arvalis</i> , 9 | id. id. | 1.259 | 0.3497 | 0.6025 |
| 8. <i>Felis domestica</i> , 10 and 11, gln. cerv. V and cocc. I | id. id. | 1.123 | 0.3119 | 0.6466 |
| 9. <i>Python</i> (species), 12 and <i>Seps chalcides</i> , 14 | id. id. | 1.187 | 0.3296 | 0.5892 |
| 10. <i>Varanus arenarius</i> , 13 and <i>Seps chalcides</i> , 14 | id. id. | 1.203 | 0.3341 | 0.5386 |
| 11. <i>Bos taurus</i> , 15 and <i>Mus musculus</i> , 16 | Rad. ant. spin. | 1.195 | 0.3320 | 0.6555 |
| 12. <i>Canis familiaris</i> , 17 and <i>Canis vulpes</i> , 18 | Purkinje cerebell. | 1.199 | 0.3330 | 0.6651 |
| 13. <i>Canis familiaris</i> , 21 and <i>Putorius putorius</i> , 22 | Gangl. cerv. sup. n. sympath. | 1.248 | 0.3466 | 0.6523 |
| | Mean | 1.204 | 0.3344 | 0.6095 |

The cells compared there are all adult, and homologous as regards their general character, but not being in each case of accurately corresponding places in the central nervous system, they cannot be directly referred to the body weights.

¹⁾ Cf. in these Proceedings, Vol. XXIII, p. 672, Table I. There on p. 674 also the above calculations were already published in Table II.

When now the power of the cell volume C , is calculated, by which the plasma volume D increases, we find for it 1.2 or $6/5$. We find 0.6 or $3/5$ for the power of the cell volume by which the nucleus volume K increases proportionally. On increase of the nerve cell the plasma volume varies, therefore, proportionally as the square of the nucleus volume. As $6/5 \times 5/18 = 6/18$ or $1/3$, the plasma volume appears to increase proportional to the third root of the body weight or $P^{1/3}$, and the nucleus volume proportional to the sixth root of the body weight or $P^{1/6}$.

Thus it appears that only the plasma, which is directly connected with the nerve fibre, in such a way that the axis cylinder passes into it, has the said direct dynamic significance. The nucleus, which is always separated from the plasma by a membrane, is directly concerned only with the life of the cell and its intern mechanism. The nucleus, in the common opinion, is the bearer of the hereditary properties in the nervous system, and it regulates the constructive metabolism, growth, and reproduction of the cell.

But still this "strange" exponent $5/18$ is only partly accounted for. Why does the volume of the nucleus K vary proportional to the sixth root of the body weight, i. e. to the square root of the body length, \sqrt{L} , or K^2 to L ?

This too I already discussed on that former occasion. The following remarks may now be added.

It has appeared chiefly from the then cited cytological researches and studies by GERASSIMOW, BOVERI and R. HERTWIG that the volume of the plasma depends on that of the nucleus: The relative size of the nucleus is determined by a dynamic state of equilibrium between the volume of the nuclear substance and the free surface of the cell, i. e. of the plasma. Further that with such a constant ratio the rate of cell division also remains constant. Now we actually see in the largest, i. e. full-grown homologous ganglion cells, in every case compared above, the volume of the nuclear substance increase in nearly quite the same relation with the body weight as the free surface of the cell, for $P^{1/6} = P^{9/54}$ and $P^{5/18} \times 2/3 = P^{10/54}$. It may, therefore, be admitted that these cells are in such a dynamic state of equilibrium. The volume of the nucleus increases, indeed, somewhat less than exactly proportional with the surface of the cell (which would be required for cell division), but in this condition of the cell it remains in equilibrium with the general dynamic condition of the body. For the metabolism of the cytoplasm increases in the same rate with the increasing volume of the nuclear substance K , and consequently the kinetic energy issuing from the nucleus proportionally to K^2 .

But we found also K^2 increasing proportionally to L or $P^{1/3}$. And this is the same ratio as exists between the mass of the body and the muscular force, the metabolism, the rate of conduction of the nerve impulses.

It has been found cytologically that with constant relation of nucleus and plasma also the rate of cell division remains constant. And already in 1895 ALEXANDER SUTHERLAND¹⁾ had shown that the time of incubation of bird species and the time of gestation of related species of mammals increases proportional to $P^{1/6}$ or $\sqrt[6]{L}$; weight and length being those of the full-grown animal's body.

In general this time is $T = n\sqrt[6]{P}$, in which n is a constant, almost the same for all bird species, but different for every order or family of the Mammalia, which tends to increase with the increase of "nerve complexity, as gauged by size and efficiency of brain". Its amount is in indubitable connection with that of the coefficient of cephalisation κ , which is determined by the heteroneuric increase of the number of nerve cells; but n certainly increases less greatly and is, in Mammalia, also dependent on other circumstances (as the non-coincidence of the dates of copulation and fecundation). The values n and κ are highest in Man, Apes, and the Elephant. The 105 bird species mentioned by SUTHERLAND differ relatively little inter se in their cephalisation, but in some its influence on the time of incubation can yet be recognized, such in the Owls in comparison with the Gallinae. Thus the time of growth, determined by cell division, to birth appears to be in the same relation to the body weight of the adult animals as the nucleus volume of full-grown homologous nerve cells, which cease dividing at birth. This means equal increase of the number of nerve cells to their separate volume. Again, finished cell division in the brain implying completion of linkage in the nervous integrative machinery, it thereby causes mechanically birth, of mammal as well as bird.

In the origination of a heteroneuric species the phylogenetic growth of the brain volume is not uniform, in simple mechanical accordance with the phylogenetic growth of the body, as in the establishment of a larger homoneuric species, but it is stronger in those most compounded parts of the brain, where new chains of cells are superposed upon the preëxisting chains, superiorly integrating

¹⁾ ALEXANDER SUTHERLAND, Some Quantitative Laws of Incubation and Gestation. Proceedings of the Royal Society of Victoria Vol. VII. (New Series), p. 270–286. Melbourne 1895. Also in The Origin and Growth of the Moral Instinct, p. 69–71 and 101–102. London 1898.

parts upon the inferiorly integrating parts of the brain. Yet the brain volumes, corresponding to equal body weights, of heteroneuric species are to each other as 1 to 2, 3 or 4, which implies that the volume of those superposed chains of cells, in the origination of a heteroneuric species, is equal to, double or triple the volume of the preëxisting chains. We may infer from this, that the phylogenetic progress of the brain, by evident discontinuous variation (mutation), after all depends on segregation of aliquot parts from polyploidly increased nuclear substance.

As, again, the size of the nerve cell body and its chief component parts is adjusted to the mechanism of the whole animal, and every nerve cell is bound to coöperation with many homologous, and non-homologous nerve cells, its relatively stable character, manifested in the ontogenetically limited, and phylogenetically infrequently, but then from the beginning definitely increased multiplication by division, becomes comprehensible, especially when — in the origination of a heteroneuric species — the multiplication must be greater in the most compounded and intricately functioning parts of the brain.

Physiology. - "A further Contribution concerning the function of the Otolithic Apparatus." By Prof. R. MAGNUS and A. DE KLEYN.

(Communicated at the meeting of May 27, 1922).

In a previous publication ¹⁾ we demonstrated that when caviae are centrifuged by WITTMACK'S method, being thereby deprived of otolithic membranes, the labyrinth-reflexes *resulting from position* (tonic labyrinth-reflexes on the extremities, "Labyrinth stell-reflexes", and compensatory eye-positions) will disappear, but that, on the other hand, the labyrinth-reflexes *responding to movement* (rotatory actions and after-reactions on head and eyes and the reflexes on progression-movements) will persist. It follows that the above position labyrinth-reflexes are otolithic reflexes, since change of position of the head in space does not enable us to elicit a *change* of the stimulation in the sensory epithelium of the otolithic maculae, but does not at all mean that the sensory epithelium cannot, under these circumstances, be in a permanent condition of stimulation. It is *a priori* quite possible that the sensory epithelium of the maculae, like that of the retina, continually produces stimuli, whose magnitude, in the absence of the removed otolithic membranes, can no more be altered by the changes of position of the head in space.

This conception was brought home to us by experiments to be published afterwards.

In order to go further into this subject we started from the following consideration:

The extirpation of *one* labyrinth in a normal animal brings about an intricate complex of phenomena. A previous minute inquiry ²⁾ into these phenomena enabled us to establish the following symptoms as resulting directly from the unilateral extirpation of the otoliths (membranes + sensory epithelium) or rather from the activity of the otolithic organs on one side only:

a. Rotation and flexion of the head towards the missing labyrinth.

b. Eye-deviation: the eye on the side of the removed labyrinth, deviating downwards, the other upwards..

¹⁾ These Proceedings, Vol. XXIII, p. 907.

²⁾ Pflügers Archiv. 154. 178. (1913).

As secondary results from the rotation of the head sub *a* appear change of posture of the whole body, difference of tonus in the extremities, rolling movements etc.

We do not know as yet which part of the labyrinth is responsible for a transitory difference of tonus in the extremities, which persists also with the head in the normal position towards the trunk. This symptom has, therefore, to be left out of consideration in the following discussion.

On the basis of these findings we performed the following experiments:

Caviae were centrifuged after the familiar method of WITTMACK. Now only those animals were used for further experimentation in which clinically all labyrinth-reflexes of position disappeared and all movement-reflexes maintained themselves, or, in other words, animals in which it could be expected that all the otoliths had been completely detached on either side.

In order to eliminate as much as possible a stimulating, or paralysing influence of the removal itself on the sensory epithelium, the animals were regularly examined and the experiment proper was started only from 7 to 9 days after the centrifugation.

In this procedure about 0.1 cc. of a 5% cocain solution was injected unilaterally through the ear-drum into the middle-ear, in order to paralyse the whole labyrinth on that side.

If it should now appear that, after the removal of the otoliths, the sensory epithelium of the maculae was not in a condition of stimulation, it could be expected that no phenomena should reveal themselves after the cocain injection, with the exception only of a nystagmus consequent on the elimination of the *semicircular canals* on the injected side.

If, however, there is indeed, after the removal of the otoliths a stimulation in the sensory epithelium of the maculae, we may look for asymmetrical phenomena after the cocain-injection, since at the injected side the sensory epithelium is completely paralysed and there is a constant condition of stimulation at the other side.

After the cocain-injection a rotation of the head towards the injected side ("Grunddrehung"; utriculus) and an eye-deviation (eye at the injected side down, the other eye upwards; sacculus.) may then be expected, i. e. phenomena agreeing with those appearing in *normal* animals, if ipsilaterally the labyrinth is paralysed through extirpation or through injection. With this difference, however, that the phenomena in animals with removed otoliths do not vary, as is the case in normal animals after unilateral extirpation of the

labyrinth, with the various positions of the head in space consequent on the varying influence of the otoliths of the unimpaired side, but that these phenomena are constantly the same whatever the position of the head of the animal under examination may be, when it is held up freely in the air.

Five similar experiments were made, which are instanced in the following three protocols:

Cavia R:

- 28/6 1921: All labyrinth-reflexes normal.
Centrifugation: head up, chest inward, time 2 minutes, rate 1000 m. per minute.
- 2/7 1921: Total lack of tonic reflexes.
- 4/7 1921: Reflexes of the semi-circular canal: rotation-reactions towards the right positive, to the left weak.
Progression-reactions: doubtful or lacking.
Total lack of tonic reflexes.
- 5/7 1921: Reflexes of the semi-circular canal (also progression-reactions) all present and symmetrical.
Tonic reflexes: all present. Sits symmetrically, no eye-deviations. In dorsal position with head in normal position to the trunk: no distinct difference of tonus in the extremities.
- 11^h 39'. 0.1 cc of 5% cocain solution into *left* middle-ear.
- 11^h 41'. Held up in the air with head down: head 90° towards the right. When sitting O D ¹⁾ down O S ²⁾ up (consequently stimulation of the left labyrinth).
- 11^h 43'. Head down: head symmetrical again.
- 11^h 47'. Head down: head 20—30° rotation to the left, slightly turned to the left. When sitting a slight levoverion of the head, no distinct eye-deviations.
- 11^h 49'. Head down, 45° levo-rotation. When sitting falls on the left side. Head in normal position: no distinct difference of tonus in the extremities. If moved on the ground to the right much greater resistance than against moving to the left, strong inclination to the left (incipient paralysis of the left labyrinth).
- 11^h 51'. Head down: 70° levo-rotation. When sitting head-nystagmus towards the right. Is moved on the ground: rolling to the left. No distinct eye-deviation.
- 11^h 54'. Head down 90° levo-rotation. OS slightly downwards. OD upwards.
- 12^h. OS weak nystagmus beats anteriorly upwards. OD posteriorly downwards. No change of the phenomena with a change of the position of the head in space.
- 12^h 3'. Marked spontaneous nystagmus, direction as at 12^h.
- 12^h 6'. Marked deviation and nystagmus, do not change with a different position of the head in space.

¹⁾ O D means Right eyeball.

²⁾ O S means Left eyeball.

- 6/7 1921: Reflexes of the semicircular canal: all present and symmetrical.
Tonic reflexes: all absent, asymmetry of cocain-test quite disappeared.
12^h. Decerebration, fair stiffness.
Shifting from ventral to dorsal position: no trace of tonic labyrinth-reflexes. Rotation of the head in lateral position: Typical cervical reflexes, no labyrinth-reflexes.

Cavia S.

- 28/6 1921: All labyrinth reflexes present and normal.
Centrifugation: head up, chest inward, time 2 minutes, rate 1000 m. per minute.
- 4/7 1921: Reflexes of semicircular canal: asymmetric reflexes. Rotation-reactions on head and eyes with rotation to the right weak, with rotation to the left strong.
Progression-reactions: weak; extension of the legs even lacking.
Tonic reflexes: lacking, only slight „Grunddrehung” to the left.
- 7/7 1921: Reflexes of semicircular canal: present and symmetrical. Progression-reactions weak but present.
Tonic reflexes: lacking, no more „Grunddrehung”. Sits symmetrically. No eye-deviation.
Dorsal position head in normal position towards the trunk; no difference of tonus in the extremities
- Injection of cocain in the *left* middle-ear.
- 12^h 30'. Held up in the air, head down: dextro-rotation of head (stimulation of the left labyrinth).
- 12^h30¹/₂'. Head down: head, in normal position, not turned.
- 12^h31'. Head down: levo-rotation of the head (incipient paralysis of left labyrinth).
- 12^h31¹/₂'. Head down: 60° levo-rotation of the head.
- 12^h33'. When sitting, head turned and flexed to the left: clock-hand movements to the left, no nystagmus.
- 12^h 34'. OS downward, OD upward; no nystagmus.
- 12^h 34¹/₂'. Marked eye-deviation, no nystagmus: no difference of deviation with change of position of head in space. Head down: head turned 90° to the left.
- 12^h 36'. Right lateral position: head in position of normal sitting animal. }
Left lateral position: head in dorsal position. } No change of the rotation of the head with different position of the head in space.
Dorsal position: head right lateral pos. }
Head up: head left lateral position. }
- 12^h 38'. No nystagmus.
- 12^h 40'. Rotation to the right and to the left: eye-rotation reaction and nystagmus.
" " " " " " " " : head rotation reaction positive.
On the ground: clock-hand-movements to the left; pushed with experimentator's foot: rolling once to the left.
- 12^h 52'. Evident eye-deviation: for the first time very strong spontaneous nystagmus. OS anteriorly upward, OD posteriorly downward.

- 4h. When sitting, head flexed and with maximum rotation to the left, marked rolling movements, strong spontaneous nystagmus.
 8/7 1921: Tonic reflex entirely lacking. Yesterday's asymmetry quite disappeared.
 9/7 1921: Animal dyspnoeic. Decerebrate rigidity not good.
 Tonic labyrinth reflexes decidedly not present.

Cavia F.

- 28/5 1921: All labyrinth-reflexes positive.
 Centrifuged with head up, chest inward, time 2 minutes, rate 1000 m. per minute.
- 31/5 1921: Semicircular canal reflexes: Rotation-reactions and after-reactions: positive.
 Progression-reactions: lift-reaction positive, the others weak.
 Tonic reflexes: lacking.
- 2/6 1921: Reflexes of semicircular canal: all positive. Tonic reflexes: lacking.
 5^h 12'. 0,05 cc. 10% cocain through left tympanum.
- 6 hour. Sitting with head placed in the normal position: OD upward, OS downward (incipient paralysis of left labyrinth).
- 6^h 2'. Sitting with head turned a little towards the left, the whole animal inclines to the left.
 Hanging with head down: "Grunddrehung" 90° to the left.
- 6^h 6'. Rotating with head *inward*, rotating to the left, weak rotation-reaction of the head, distinct after-reaction Dextro-rotation: marked rotation-reaction of the head and no after-reaction.
- 6^h 7'. Eye-rotation reactions: dextro rotation, distinct reaction with nystagmus, no after-reaction. With levo-rotation: reaction and afterreaction.
- 6^h 10'. Progression-reaction: Liftreaction not distinct.
 "Springing reflex" positive.
 Muscular tremor: positive in all directions except posteriorly.
 Tonic labyrinth-reflexes negative.
 Position of the head in the air with:
- | | | |
|---|---|---|
| Right lateral position: head in normal position to the trunk through "Grunddrehung", often hangs down. Left lateral position: head in dorsal position through "Grunddrehung". Head up: head in left lateral position, animal now becomes restless (cocain-action). Head down: head turns 90° to the left. Dorsal position: head in right lateral position. through levorotation, often also in dorsal position with left flexion. | } | Ergo constant rotation of the head, which does not change with change of position of the head in space. |
|---|---|---|
- 6^h 18'. When sitting with head placed in the normal position: OD anteriorly upward, OS posteriorly downward. Nystagmus just the opposite way.
- 6^h 33'. Right lateral position: OS posteriorly downward, nystagmus the opposite way. Eye-deviation and nystagmus of the left eye are the same with right and left lateral position of the head and equally strong; the same holds good also for OD.

- 7/6 1921: Animal sits symmetrically, no eye-deviation.
 Reactions of semicircular canal: all positive.
 Tonic reflexes: all lacking. Asymmetrical phenomena quite gone as in cocain-test.
- 8/6 1921: Like previous day. When sitting, head sometimes turned very slightly to the right, for the rest animal sits symmetrically, no eye-deviations.

Anatomical examination by Dr. M. DE BURLET. All otolithic membranes detached.

- Right sacculus; sensory epithelium without membrane; the otolithic membrane isolated in the sacculus between ductus endolymphaticus and the back-part of the sensory epithelium.
- Right utriculus; sensory epithelium without membrane; the otolithic membrane lies between the posterior portion of the macula and the entrance to the crus commune.
- Left sacculus; sensory epithelium without membrane: the otolithic membrane rests against the lateral wall of the sacculus and above the macula.
- Left utriculus: sensory epithelium without membrane; the otolithic membrane is detached towards the inner side and above the macula but lies in the utriculus.

These experiments go to show that for more than a week after the removal of the otolithic membranes the sensory epithelium is still in a constant condition of stimulation. When one labyrinth is for some time eliminated by cocain, the stimuli emanating from the non-injected labyrinth will induce asymmetrical phenomena, similar to those after unilateral extirpation of the labyrinth in normal animals, with this difference, however, that in the centrifuged animals injected unilaterally with cocain, these phenomena do not change with a *change* of position of the head in the air.

Considering that there was a week's wait after the centrifugation, it is probable that the above condition of stimulation should no longer be ascribed to centrifugation, and that, therefore, to the sensory epithelium of the maculae the power should be assigned of eliciting stimuli, which, owing to the absence of the otolithic membrane, do not vary much as to strength.

The function of the otolithic membranes, then, consists in altering the intensity of this condition of stimulation of the sensory epithelium. This stimulation will be stronger or weaker according as the membranes pull at the epithelium or press upon it.

Relative to the portion of the sacculus (the main part) innervated by the N. saccularis it has been previously demonstrated that the stimulation decreases with pressure and increases with pulling. This mechanism exists probably also for the utriculusmaculae.

It appears that for the division of the sacculus (sacculus corner) innervated by the N. utricularis the relations are more intricate.

Our results may perhaps be conducive to the proper conception of the function of the sensory epithelium of the otolithic maculae.

The above-named property of the otolithic apparatus to elicit continuous stimuli even after the otolithic membranes are detached — as here described — undoubtedly demands attention in the further study of the unilateral affection of these organs.

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Geology. — „*Cuba, The Antilles and the Southern Moluccas.*” By
L. RUTTEN.

(Communicated at the meeting of May 27, 1922).

In 1865 E. SUESS endeavoured to show in which way North-, and South-America are connected geologically ¹⁾. Basing upon the then scant geological literature of the borderlands, he partly adopted the conceptions of some few of the older explorers. He observed that the mountain systems of Western North-America do not directly merge into those of Western South-America, but that in South-Mexico and in Guatemala the coastal ranges bend round, ramifying there in different chains, which cross transversely the narrow Central America, to proceed on their course in the Greater Antilles. All along the row of the Antilles SUESS imagined to observe the traces of a large chain of folded-mountains, which he conceived to extend along the North Coast of South America, as far as the boundary of Venezuela and Columbia to merge there into the Andes. So he considers the Andes of South-America as a continuation of the mountains of Western North America, but looks upon the curving chain of mountains via the Antilles as the connecting link.

In the region of the Antilles SUESS distinguished three zones: an interior zone of small islands all composed of young volcanic rocks with very young coastal limestones and allied formations, extending from Grenada to Saba; a middle zone, in which in many places older, folded rocks emerge, building up the Antillean-Cordillera proper, extending from Trinidad via Barbados as far as Haiti, branching out there in at least two chains, of which the southmost proceeds via Jamaica to Honduras, while the most northern runs via Cuba to Yucatan; lastly an exterior zone, stretching from Barbuda via the Bahama Islands and Florida to Yucatan and which is supposed to be the remainder of the unfolded and disrupted “Vorland” of the Antillean Cordillera.

Already SUESS had pointed to the striking analogy between the row of the Antilles and the Southern Moluccas. A few years later

¹⁾ E. SUESS, *Das Antlitz der Erde*. I. 1885.

this analogy was discussed further by WICHMANN¹⁾ and MARTIN²⁾. In the Southern Moluccas we also distinguish an interior curve of volcanic islands, an intermediate curve, consisting of the remains of folded mountains, and farther to the east the remainder of the almost undisturbed "Vorland".

In many points the hypothesis of SUESS has been corroborated by subsequent researches. K. SAPPER³⁾ has demonstrated that the peculiar curvature and ramification of the tectonical units in Northern Central America, which SUESS only suspected, really exist. W. SIEVERS⁴⁾ has proved it to be probable that the eastern Cordilleras of Columbia split up in the North into different branches, then bend round to the North-east and to the east, and can be traced as far as Trinidad with rather great distinctness. LACROIX⁵⁾ found in young volcanic rocks of Martinique xenoliths of mica-schist, proving thereby that in the subsoil of this island there still must exist old, metamorphic sediments. HÖGBOM has pointed out the remarkable analogy⁶⁾ between the eruptive rocks of the Virgin Isles and those of the Andes of South-America. In the collections of the chemist RICHARD LUDWIG W. SIEVERS has found a young eruptive rock from Alta Vela, a small island south of Haiti, and has proved the possibility that this islet may be the continuation of the volcanic interior curve of the Lesser Antilles⁷⁾. Finally W. BERGT⁸⁾, who arranged the above-named collections petrographically, has shown the occurrence of old schists in Haiti. Lastly DE LA TORRE⁹⁾ discovered in Western Cuba a fauna of Malm-ammimonites and M. SANCHEZ ROIG¹⁰⁾ established that this fauna bears a close resemblance to the jurassic fauna of San Pedro del Gallo in Mexico, which has been treated in such a masterly way by BURCKHARDT¹¹⁾.

On the other hand SUESS's theory has not been universally accepted

1) C. E. A. WICHMANN, Samml. Geol. Reichsmus. II, 1887, p. 198 sqq.

2) K. MARTIN, Tijdschr. Kon. Ned. Aardr. Gen. VII, 1890, p. 260 sqq.

3) K. SAPPER, Peterm. Geogr. Mitt. Erg. Hefte 127, 1899, 151, 1905; Report 5th Int. Geogr. Congr., held in the Un. States, 1904.

4) W. SIEVERS, Peterm. Geogr. Mitt. 1896, p. 125—129.

5) A. LACROIX, La Montagne Pelée et ses éruptions, 1904.

6) A. HÖGBOM, Bull. Geol. Inst. Upsala, VI, 1905.

7) W. SIEVERS, Zeitschr. Ges. für Erdkunde Berlin, 33, 1898.

8) W. BERGT, Abhandl. Gesellschaft Isis. Dresden. 1897, p. 61—64.

9) C. DE LA TORRE, C.R. Congrès Intern. Géol. XI, Stockholm, 1910, p. 1021—1022.

10) M. SANCHEZ—ROIG, Boletín especial de la Secretaría de agricultura, comercio y trabajo, Habana, 1920.

11) C. BURCKHARDT, Bolet. Instit. Geologico Mexico, 29, 1912.

in America. The investigations of Americans have negated rather than substantiated SUSS'S conceptions in some respects. J. W. SPENCER¹⁾, for instance, came to the conclusion, chiefly after the study of charts and morphological speculations in connection with them, that the Antilles were not the remains of an old cordillera. This researcher maintained that the whole tract of the Caribbean Sea, the Antilles and the Gulf of Mexico constituted an ancient continental region, which ever since the Miocene had executed the most stupendous vertical fluctuations of an amplitude of many thousands of meters. R. T. HILL²⁾, however, who visited many of the Antilles, is by no means inclined to consider most of these islands as other than true oceanic formations and refuses to believe that there is any connection between the northern Antilles and Barbados-Trinidad, the latter being by him assigned to the South-America mainland. In his aversion to the assumption of old-sedimentary cores in the Antilles east of Western Cuba he even goes the length of questioning the results of BERGT (l.c.) who had established the occurrence of old schists in Haiti on the basis of simple petrographic work.

Neither were the long-continued explorations of T. W. VAUGHAN³⁾, who has contributed so largely to the knowledge of the geology of Central America in modern time, based upon the ideas of SUSS, which, as shown above, were of such pregnant significance for many a European explorer.

Particularly the island of Cuba, where since the Spanish-American war a number of American explorers have been working, seemed to have many features not belonging to the other Antilles. The Spanish mining-engineer SALTERAIN already had mistaken a group of sharply folded rocks from the environs of Habana, where fossils had never been found for cretaceous sediments⁴⁾ and the later American⁵⁾ explorers adhered to this view or contended it only

¹⁾ J. W. SPENCER, *Geol. Magazine* (4), I, 1894, p. 448—451; *Bull. Geol. Soc. America* VI, 1895, p. 103—140; *Transactions Canad. Instit.*, V, 1898, p. 359—368, and many other publications.

²⁾ R. T. HILL, *Bull. Museum. Comp. Zoology, Harvard Coll.*, 34, 1899, p. 225 sqq.; *Bull. Geol. Soc. America*, XVI, 1905, p. 243—288, and many other publications.

³⁾ T. WAYLAND VAUGHAN, *Bulletin U.S. National Museum, Washington*, 103, 1919; *Contributions to the geology and paleontology of the West Indies*, publ. by the Carnegie Inst. of Washington, 1919, in which older publications are cited in extenso.

⁴⁾ P. SALTERAIN, *Boletín Mapa geológico de España*, VII, 1880.

⁵⁾ R. T. HILL, *Amer. Journal of Science*, (3), 48, 1894, p. 196—212. *Bull. Mus. Compar. Zoology Harvard Univ. Geol. Series II*, 1895, p. 243—288; B. WILLIS, *Index to the stratigraphy of North America*, U.S. Geol. Survey, *Profess. Papers*, 71, 1912.

reservedly¹⁾. However, the petrographic habitus of this would-be cretaceous formation, made up of white limestones, of soft, white marls and of loose calcareous sandstones, is quite different from all the cretaceous rocks known from the other Antilles, Central America and Northern South-America, so that Cuba seemed to be isolated from the rest in this respect. Another peculiarity of Cuba seemed to be that on the whole the tertiary is not very thick and only feebly folded: HILL²⁾ says that the tertiary is merely a thin veneer overlying the older formations so that its thickness does not excel 1000 feet, and HAYES-VAUGHAN-SPENCER have reproduced profiles of the island in which everywhere a very feebly folded tertiary formation is marked³⁾. If this is correct, Cuba differs very much from the other Antilles, for in Haiti⁴⁾, Barbados as well as in Trinidad⁵⁾ there are very thick and intensely folded tertiary deposits, as may be expected in a young mountain-range, such as SUESS asserts the Antilles to be composed of.

A two months' stay in Cuba, in the months of March and August of the past year, put me in a position to explain this seeming contradiction and to detect some striking resemblances between Cuba and the other Antilles.

First of all the so-called cretaceous deposits in the environs of Habana were explored. They can readily be examined in numerous exposures along roads and railway cuts in and near the capital. They are composed of white soft, sometimes nodular, fine-grained marls; of light-coloured, youngish looking, organogenetic limestones, which are seldom very pure, most often however contain some volcanic tuff-material; of true submarine tuffs; while sometimes also peculiar fine-grained limestone-breccias occur in the formation. In numerous spots I found in the limestones and in the submarine tuffs micro-organisms, which could be determined in microscopical sections. It now appeared that besides a number of Foraminifera, insignificant for the age of the formation, and besides Lithothamnium,

1) C. W. HAYES, T. W. VAUGHAN and A. G. SPENCER, *Geology of Cuba*, 1901 reprinted in 1918 by the Dirección de Montes y Minas at Habana.

2) R. T. HILL, l.c.

3) C. W. HAYES, T. W. VAUGHAN and A. G. SPENCER, l.c.

4) L. TIPPENHAUER, *Peterm. Geogr. Mitteilungen*, 1899, p. 25—29, 153—155, 201—204; 1901, p. 121—127, 169—178, 193—199; 1909, p. 49—57. W. F. JONES, *Journal of Geology*, 26, 1918, p. 728—758.

5) I. B. HARRISON and A. J. JUKES BROWN, *The geology of Barbados*, 1890, and other publications. G. WALL and J. SAWKINS, *Report on the geology of Trinidad*, *Memoirs Geol. Survey*, London, 1860.

also small Nummulinae and Orthophragminae occur in various localities and Nummulinae and Lepidocyclinae in other places. I encountered in various tuffish limestones between Ardaí and Arroyo Naranjo small Nummulites and Orthophragminae, while in limes, south-east of Regla, to the south of the bay of Habana and to the north of Guanabacoa, besides Nummulites also small Lepidocyclinae were found, which also occur in the railway-cut, north-east of Palatino (the finding-places are marked on the accompanying map).¹⁾ This "Older Habana-formation" is intensely folded, with dominant W—E. strike, and rapidly alternating steep dips, so that no positive opinion can be formed about the thickness of the whole complex of layers with its few well-continuous sections. This thickness however is sure to be very considerable. It is evident that this formation, which contains Nummulites and Orbitoides, and which, in concurrence with SALTERAIN (l. c.) was generally mistaken for cretaceous, is of a distinctly more modern type, being nothing else but the well-developed and intensely folded eogene, which we recognize with the same tectonic and partly also with the same petrographic features in so many localities of the Antilles. The occurrence of Orthophragmina implies that part of this intensely folded formation is decidedly eocene. We will endeavour to ascertain whether perhaps subsequent parts of the Tertiary are represented in this complex.

If the fossils, occurring in the "Older Habana-formation", had been found in Europe or Asia, there would be no doubt whatever about the occurrence also of oligocene and maybe even of old-miocene rocks in this complex, as in Europe as well as in Asia Lepidocyclinae are characteristic of the oligocene and the older miocene (Stampian to Burdigalian). However, in America Lepidocyclinae have been found also in unmistakably eocene deposits,²⁾ so that their occurrence in the vicinity of Habana is in itself no evidence at all. Now, the American species in positively eocene rocks (south-eastern part of the United States), are all large species, except one (*L. floridana* Cushman with a diameter of 4—8 mm.). In San Bartholomew (*L. antillea* Cushman with 5 mm.) and in the zone of the Panama-canal (*L. Macdonaldi* with 5—7 mm.) there occur, it is true, some smaller species in rocks, taken to be eocene, but the age of these deposits is not so well established as that of the

¹⁾ It is a pity that the names in the map are rather illegible but with the aid of a reading-glass it will be possible to recognize most of them.

²⁾ J. CUSHMANN, U. S. Geological Survey, Professional Paper, 125 D, 1920.

T. W. VAUGHAN, Proceedings First Pan Pacific Conference, Honolulu, 1921, p. 754—755.

formations of the South-east of the United States. Now, in the Habana rocks, described above, large *Lepidocyclinae* are absolutely lacking; they contain only dwarf-species which — as experience in Asia and Europe has taught us — are more or less indicative of younger formations, so that part of the “Older Habanaformation” must very likely still be referred to the Oligocene. And this is not all. In the city of Habana and west of it the Older Habanaformation is overlain by rocks of quite similar petrographic habitus, but they are much less disturbed. These rocks of the „Younger Habanaformation” (organogenetic limestones, white and yellow marls, submarine tuffs) form namely a monocline, whose core still exhibits steep dips — up to 40° and higher —. The younger portions of this formation, however, which in its totality is dipping towards the sea, are much less steep. In the suburb of Vedado the marls of this formation are overlain by coral-limestones which are also dipping down towards the sea. The rocks of this “Younger Habanaformation”, which are so beautifully exposed in the marlpits of Puentes Grandes and of Cienaga and at the Castillo del Principe, are lying unconformably — as the accompanying map indicates — on the rocks of the “Older Habanaformation”: while the strike of the older rocks is E.—W., that of the younger is about N.E.—N.N.E. The facts, however, that in the deeper parts of the younger formation the layers are very sharply inclined, and that there is a remarkable petrographic similarity between the two formations tend to show that the stratigraphical gaping between the two formations is only very inconsiderable; nay, in all probability, the unconformity is only “tectonic”, is originated during the folding, and the two formations succeed each other most likely without a significant stratigraphical gap.

Now, M. SANCHEZ ROIG¹⁾ has for several years been collecting fossils from the marlpits of Cienaga. It is especially the teeth of *Selachii* that were encountered here. They point to a miocene age, while the more southern limestones of Vedado belong even to the Pliocene.

The foregoing no doubt justifies the conclusion that the rocks of the “Older Habana formation” belong partly to the eocene, partly to the oligocene, that the tertiary orogenetic movements in this part of Cuba began towards the close of the Oligocene, and that they continued even in the Pliocene.

So while in the North the layers of the “Older Habanaformation” are overlain unconformably by miopliocene rocks, which have still

¹⁾ M. SANCHEZ ROIG, Boletín de Minas, Habana, N^o. 6, 1920.

co-operated in the crustal movements, in the South near Arroyo Narranjo limestones are overlying the "Older Habanaformation", which are perfectly horizontal and can be traced southward as far as Guira, invariably in horizontal position. Near Arroyo Narranjo these limestones, which in their habitus differ greatly from the rocks of the "Older Habanaformation", are coastal limestones; farther to the south also *Globigerina* limestones occur. As a matter of fact these limestones, which have had no share in the latest orogenetic movements, must be of more recent date than the miopliocene rocks of the "Younger Habanaformation" and belong consequently to the Youngest Pliocene or Pleistocene. These limestones, which the Geological survey-map of North-America¹⁾ still marks as Old Tertiary, have lent support to the opinion that the Cuban Tertiary is only feebly folded, and that the Tertiary constitutes only a thin varnish overlying the older formations.

This does away with the seeming contrasts between Cuba and the other Antilles and replaces the island in the homogeneous range of the Antillean Cordillera.

In an excursion to San Diego de los Baños, about 100 k.m. to the west of the capital I encountered also here a well-developed and intensely folded eogene formation; to the North of this small town mesozoic limestones emerge, but farther to the south intensely folded rocks (strike E.-W.) are exposed everywhere — especially submarine tuffs — containing *Lithothamnium*, *Nummulites* and *Ortho-phragminae*. *Globigerina* marls also occur.

The Petrographic composition of the Cuban Tertiary is interesting also in other respects. First of all, in the Older as well as in the Younger Habanaformation limestones occur that, being examined microscopically, appear to contain much young volcanic material, nay in many cases, even change into true calcite-poor, submarine tuffs. Sharp angular splinters of plagioclase and quartz are numerous. Likewise numerous grains present themselves, of a substance containing plagioclase microlites, granules of ore and glass, which are to be considered as ground-mass fragments of an andesitic or dacitic rock. Similar eogene, submarine tuffs were also recognized in the Tertiary of San Diego. Much volcanic material also occurs in miopliocene deposits of a shallow sea (coralligene limestones, marls, calcareous sandstones and finely granular conglomerates), which are excellently exposed in the Yumurí cleft near Matanzas, about 75 k.m. east of Habana. On the contrary volcanic material seems to be lacking entirely in the very young, horizontally disposed limestones

¹⁾ B. WILLIS, l.c.

found near Arroyo Naranjo, Rincón, San Antonio de los Baños and Guira. In one of the younger portions of the Yumurí cleft-profile feldspars were so numerous that they could readily be examined in the pulverized rock. All the splinters that were examined, had a higher refractive index than canada balsam, so that there is a complete lack of orthoclase and albite. Among 20 splinters examined 13 had a higher, 7 an equal or a lower refractive index than eugenol (1.546), so the latter belong to oligoclase. Nearly all the splinters have a lower refractive index than nitrobenzol (1.556), so that among the larger feldspar splinters, which are of course fragments of phenocrysts from the dacitic-andesitic rocks, from which also the ground-mass originates, no plagioclases occur that are more basic than andesine¹). The effusive rocks supplying the material for submarine tuffs, must then have been a highly acid, potassium-poor dacite i.e., a rock in all points of the type of the "Pacific Rock".

It should be observed that the fragments of the ground-mass occurring in the tuffs, very often have a diameter of 1 mm. It is not out of the bounds of possibility of course, that similar volcanic material could have reached Cuba during an eruption of rather remote volcanoes, if at the time of the eruption a violent storm had been blowing in the direction of the island. The coarseness of the fragments, however, together with the very high frequency of volcanic material in formations extending from the eocene into the pliocene in localities nearly 200 k.m. apart, indicate that this material has not "come over" under "peculiar" circumstances from far-away volcanic centra. These submarine volcanic tuffs that are so widely diffused both stratigraphically and geographically, must be regarded as evidence that in the Tertiary the volcanic activity in the Antillean region extended over a much larger area than at present and that it did not settle down before the close of the Tertiary. This fact also tends to strengthen our view that the Antilles are geologically homogeneous.

It is likewise deserving of note, that no remains whatever are to be found of the volcanoes that must have existed as late as the latter half of the Tertiary in the neighbourhood of Cuba. This proves that already since the beginning of the Tertiary Cuba must have been subject to violent disturbances, where denudation destroyed rapidly what had been built up by volcanic and orogenetic processes.

¹) The refractive indices of the fluids used in the Utrecht geological institute for the determination of the refractive indices of minerals, have been verified only a short time ago by Prof. SCHOORL for which we tender our thanks.

Presently we shall see that other facts also corroborate this hypothesis.

In the vicinity of Habana a deeply weathered serpentine-massif (see sketchmap) has long (SALTERAIN l. c. and others) been known. In two localities — south of Guanabacoa and due south of the bay of Habana — quartzamphibole diorites are found as a dyke. These moderately acidic plagioclase rocks forcibly reminded me of the granular crystalline rocks of the "Pacific type", described by HÖGBOM (l. c.) and derived from the Virgin Isles. The felspars of this quartz-amphibolodiorite all had a refractive index higher than canada balsam, but the refractive index of most of them was lower than that of quartz, to which they often are contiguous in the microscopical sections. Consequently they belong to the acid portions of the plagioclase series. Indeed the fact that this rock is poor in potassium and comparatively rich in silicic acid (much quartz and many acidic plagioclases) reminds us forcibly of many "Andes-rocks". Also by the occurrence of granular rocks of this type Cuba is united to the American continent on the one side and on the other to the Virgin Isles.

When perusing the literature concerning the Antilles we are impressed with an other incongruity between Cuba and the other Antilles. Already long ago young Radiolaria-bearing deposits became known in Barbados (HARRISON and JUKES BROWN, l. c.) which many geologists regard as true deepsea-deposits. R. T. HILL also described tertiary Radiolaria-deposits in the east of Cuba (Baracoa). However, whereas in Barbados the Radiolaria deposits overlie unconformably the older tertiary — which developed there as a terrigenous deposit — and have only been subject there to faulting and not to folding, the Radiolaria deposits of Baracoa have a steep dip, so that there seemed to exist a stratigraphical incongruity between these deposits in the two islands. In the neighbourhood of Habana I encountered Radiolaria-bearing rocks in two levels of the Tertiary. In the first place white marls in the "Older Habanaformation" near Cerro, with a dip of 75° southward. They are entirely filled up with Radiolaria that belong for the major part to the Spumellaria, for a small part however also to the Nasselaria (fig. 1). Secondly, in the most recent part of the "Younger Habanaformation", i. e. in the marlpits of La Cienaga, white Globigerina marls occur which contain a not inconsiderable amount of Radiolaria. Now it is very well possible that the Radiolaria-marls of Cerro are the equivalent of those of Baracoa in East-Cuba, whereas the Radiolaria-bearing Globigerina marls of La Cienaga are stratigraphically more like the deposits in Barbados. Also the contrast which apparently exists in

this respect between Cuba and some of the other Antilles finds an explanation in the above.

Indications of the homogeneity of the row of Antilles can also be found in the older formations of Cuba. As stated previously, of late years Malm-ammonites have been found near Viñales, in the most western part of Cuba. These Upper-jurassic layers, which dip away to the North at a rather small gradient, are overlain by thick, old-looking grey limestones with intermediate layers of sandstones, which, therefore, are probably to be referred to the Cretaceous system. In one place I found in these limestones small nests of red chert; under the microscope this red chert appeared to be a true Radiolarite, very much like the Radiolarites so widely diffused in the mesozoic rocks of the southern Moluccan-cordillere (fig. 2). The geological institute at Utrecht possesses a number of rocks from the islands of Curaçao, Bonaire and Aruba, collected by Dr. I. BOLDINGH. Among the rocks from Bonaire and Curaçao it was not difficult to recognize Radiolarites — probably mesozoic — bearing close resemblance to those from Cuba.¹⁾ This is not all. In the coral-limestones of the Yumurí-cleft near Matanzas coarse elastic material was found; boulders to a maximum of 7 mm. in diameter. Four of them were ground, of which two appeared to be red radiolarites like those found to the north of Viñales, while in our days mesozoic sediments are lacking in this part of the island.

It is evident, therefore, that such a peculiar sediment as the mesozoic, red radiolarite is found at the extremities of the Antillean region: in the most western part of Cuba and in Bonaire and Curaçao. This, no doubt, warrants the assumption that the Antillean region is one continuous whole, parts of which, in spite of their different appearance, have many features in common, that point to an historical homogeneity.

From the occurrence of much volcanic material in the whole tertiary of Cuba, in the neighbourhood of which no volcanoes exist any more, we may conclude that the island must have been subject to great geological disturbances in recent times. A similar conclusion may be deduced from the great abundance of boulders of cretaceous Radiolarites in the miopliocene of the Yumurí-cleft, as these boulders

¹⁾ K. MARTIN, Bericht über eine Reise nach Niederl. West Indien, II, 1888, p. 28 and 73 and J. H. KLOOS, Samml. Geol. Reichs-Museums, Leiden II, 1, 1887, already demonstrated the occurrence of Radiolaria-bearing rocks in Curaçao and Bonaire. From their descriptions it is not evident, however, that we have to do here with typical Radiolarites, which at that time did not receive so much attention from geologists as nowadays.

point to a powerful post-eocretaceous mountain-building by which the deep-seated Radiolaria-deposits were uplifted beyond the sea-level, while in the Tertiary the mountains were entirely denuded again.

In the foregoing Radiolaria-bearing deposits have been described from three levels of the series of sediments of Cuba: a fourth level can still be added. Between Bacuranao and the boring-field which is located to the north of this village, green sediments were observed in the centre of the serpentine-area. These sediments are distinctly seen to dip away below the serpentine. Under the microscope they appeared to be in part volcanic tuffs, in part remarkable radiolarites, which consist chiefly of skeletons of Radiolaria, but also contain spiculae of sponges, while the silicic acid of the Radiolaria as well as of the sponges spiculae is still perfectly amorphous (fig. 3). These siliceous sediments are closely connected with the volcanic tuffs; not only do the Radiolaria-layers and the tuffs possess equal dip and equal strike, but sometimes the siliceous sediments contain splinters of plagioclase, and in one of the microscopical sections the tuff even passes into the siliceous sediment. These Radiolarites of Bacuranao certainly belong to an older level than the tertiary Radiolarites, as the former dip away below the serpentine, whereas the whole tertiary is more recent than the serpentine, whose water-worn fragments are found here and there in the tertiary limestones and calcareous sandstones. They belong moreover to another level than the red Radiolarites of Viñales and Matanzas, for the thick limestones bearing the red Radiolarites of Viñales are not found near Bacuranao. The siliceous sediments are closely related to the Cuban serpentines.

Now it is very remarkable that in Cuba such extreme deposits as Radiolarites appear in four different levels. Even when not assuming that Radiolarites are true deepsea deposits, we must be convinced that the formation of these calcium-free or calcium-poor siliceous sediments requires conditions that do not exist in the shallow epi-continental seas. At all events the occurrence of these deposits in at least four levels of the island of Cuba justifies the conclusion, that the area in which the island is now situated, was in the latter half of the Mesozoicum an extremely restless region, where now deposits of a shallow epicontinental sea (sandstones in the Chalk, Nummulites and Orbitoide-bearing limestones in the Tertiary), then again such peculiar sediments as Radiolarites¹⁾ could be formed.

¹⁾ One more fact may be adduced to confirm the conception that at least one level of the Radiolaria-bearing deposits in Cuba is formed, if not in a true deep-

There are, indeed, two more arguments for the conclusion that Cuba has ever been a very inconstant region, at least since the Tertiary.

In the outset we reminded the reader that already SUESS, WICHMANN and MARTIN had pointed out the analogy between the Antilles and the southern Moluccas, which analogy is brought out in a similar arrangement of the tectonic elements. Two points have been discussed above to emphasize this analogy. In the first place the occurrence of Red Radiolarites, so very typical of the Mesozoicum of the Moluccas, in the two extremities of the Antilles. In the second place the conception that in the latter geological periods the Antillean region was so extremely restless. It is known, indeed also of the southern Moluccas, that their region was very changeable, and was characterized by great instability in the relations of land and sea: also there the formation and the denudation of mountains took place in such rapid succession, that it is difficult to disentangle the development of the geological history. We may add even one more detail in comparing the instability of the Antillean region with that of the southern Moluccas. In the Antilles it struck us that in one and the same island Radiolaria-deposits occur at least in four different levels. Why, also of the island of Rotti, near Timor, BROUWER has described¹⁾ Radiolaria-bearing deposits in three totally different levels: Upper Trias, Malm and Tertiary.

Utrecht, May 1922.

sea, anyhow in a sea of considerable depth. In the white marls of La Cienaga, where many Globigerina and also numerous Radiolaria occur Sanchez-Roig (l.c.) has found numerous teeth of Selachii. A large number of these teeth (though by far not all) display the peculiarity that only the enamel of the teeth is left, while the dentin has completely disappeared. This state of preservation is exclusively characteristic of Selachii-teeth that are encountered in the deepest sea and in deepsea deposits.

Gf. MOLENGRAAFF and BEAUFORT, Proceedings XXIX, 1921, p. 677—692.

¹⁾ H. A. BROUWER, De Nederlandsche Timor Expeditie, III, 1921. Geologische onderzoekingen op het eiland Rotti.

DESCRIPTION OF THE PLATES.

- Fig. 1. White Radiolariamarl. Older Habanaformation. $\times 26$.
 Fig. 2. Red Radiolarite. Viñales. $\times 26$.
 Fig. 3. Silicious rock with Radiolaria and Sponge-spiculae. Bacuranao. $\times 26$.
 Fig. 4. Geological Sketchmap and transverse profile of the vicinity of Habana.
 — . — . — Railways.
 ABC—CD Line of Profile.
 S. Serpentine.
 D. Quartzhornblendediorite.
 A. Petroleum Rigs.

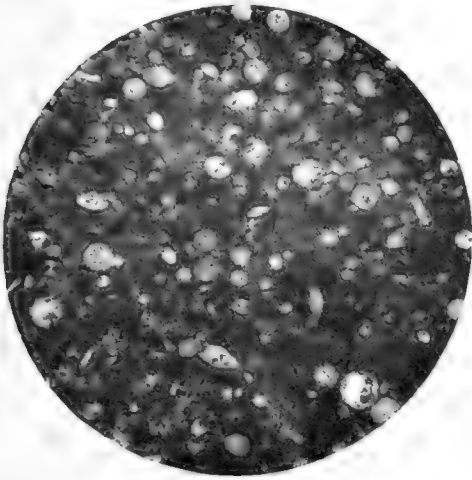


Fig. 1. $\times 26$.

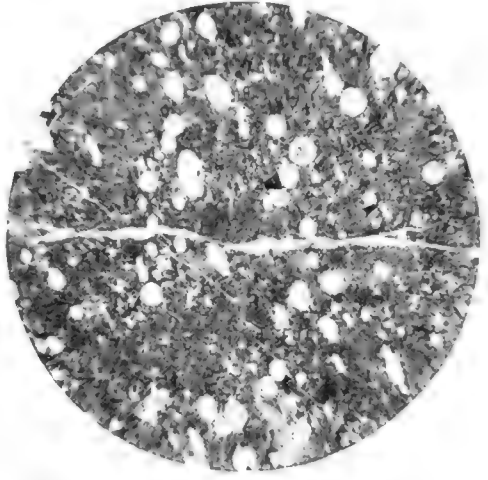


Fig. 2. $\times 26$.

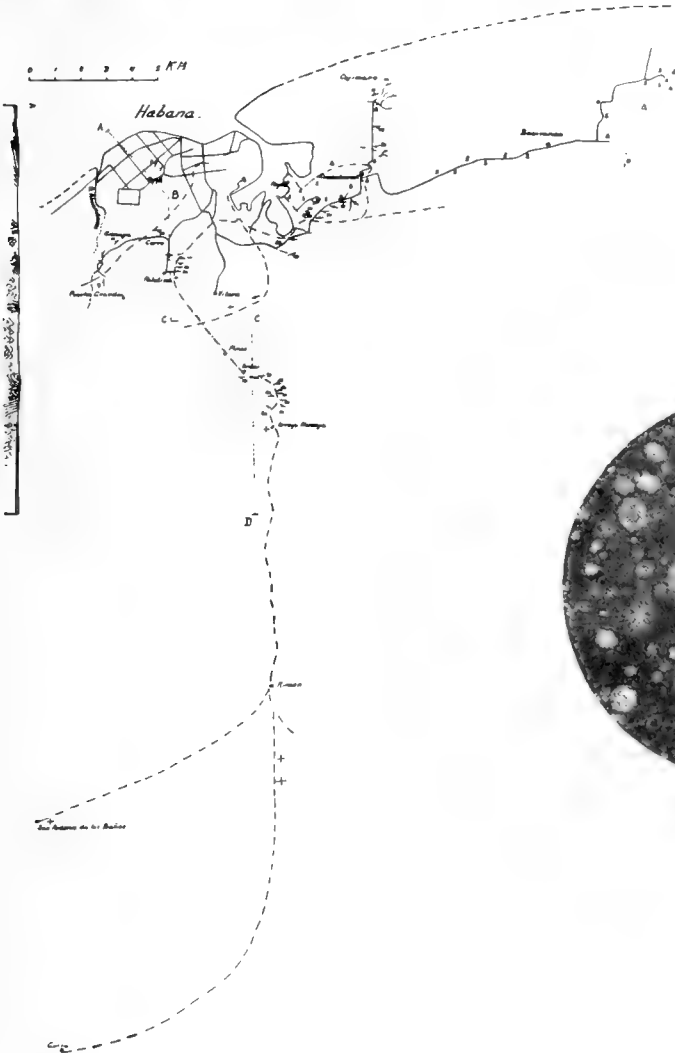


Fig. 4.

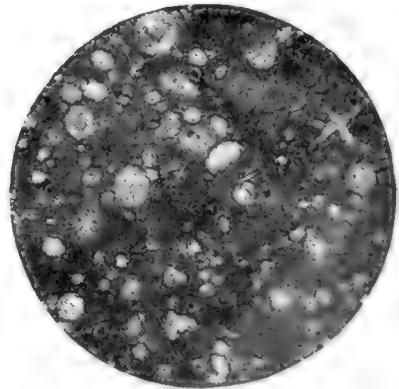


Fig. 3. $\times 26$.



Bio-chemistry. — “*Changes in Milk due to Sterile Inflammation of the Udder.*” By Prof. B. SJOLLEMA and J. E. VAN DER ZANDE.
(Communicated by Prof. C. EYKMAN.)

(Communicated at the meeting of May 27, 1922).

The examination of a number of samples of abnormal milk from cows suffering from clinically observable affections of the udder, as well as from cows in which clinically no anomalies of the udder were noticeable, impressed us in 1921 with the idea that too great an importance is ascribed to streptococci as causative agents of the secretion of abnormal milk. We found for instance that in very abnormal milk streptococci are often absent.¹⁾ We, therefore, decided to go further into this subject and produced sterile inflammation of one of the quarters (R. F.) of the udder of a milch-cow in full lactation, with the aid of a suitable injection. On the suggestion of Prof. PAIMANS a solution was administered of silver-nitrate of 0,2 %.²⁾

In the same cow a sterile abscess had previously been developed through injection of oil of turpentine in the region of the neck with a view to ascertain whether such a sterile inflammation exerted any influence on the secretion of milk. We were induced to do so, because in a previous investigation in our laboratory anomalies had been found in the milk yielded by animals which were affected by inflammation of quite other parts of the body than the udder.

The results obtained after the injection of oil of turpentine need not take us long. Although a considerable abscess had developed, the composition of the milk did not undergo a notable change, neither during the development, nor after the abscess had become mature.

Once the sediment of the milk from one of the quarters had increased a little, of which the abscess may not have been the

¹⁾ Our report pertinent to the matter in question appeared in *Tijdschrift voor Vergelijkende Geneeskunde* enz. Band 7 1922.

²⁾ We were in a position to prosecute this inquiry thanks to the aid of Prof. W. J. PAIMANS and the Conservator for Obstetrics, Mr. J. A. J. M. KIRCH, whose assistance we acknowledge with gratitude.

cause. It would seem, therefore, that a sterile inflammation does not affect the secretion of milk in the same way as a bacterial inflammation has in our earlier researches repeatedly proved to do; this result could be expected.

The effect of the sterile inflammation of the udder with silver-nitrate solution was quite different. The very next day (9 March) the composition of the milk had changed very much, as was also the case on the following days, when the milk presented also a very abnormal aspect.

Gradually composition and aspect improved; however, this quarter became choked before the milk was quite normal; at all events not a trace of milk could be drawn on March 19 and following days. The examination of the milk-samples gave the results tabulated on the following page. For the sake of comparison we have also tabulated the figures of some abnormal milk-samples *with* (N°. 164 and 142) and *without* (N°. 181 and 267) streptococci, which samples were examined in 1921. For the same reason we included the figures obtained from the same quarter (R. F.) of the injected cow before this treatment (N°. 343 and 337) and from other quarters (N°. 385 and 381) after the injection.

The table shows that the milk from the quarter injected with silver-nitrate possessed, — with the exception of the presence of streptococci, — all the properties of milk from animals, suffering in a high degree from udder-affections e.g. streptococci mastitis). Acidity, p_H , sediment after centrifugation in Trommsdorff-tubes, leucocytes, chlorin-, and lactose-content, were all changed in the same measure,¹⁾ as were also the total protein-content and the calcium-content.

Furthermore the content of total, combined-, and free carbonic acid appeared to have increased, just as in milk from cows with diseased udder. This anomaly and its connection with the hydrogenions concentration of milk has been pointed out in 1919 by L. L. VAN SLIJKE and J. C. BAKER²⁾.

Lastly, the tryptophane-content appeared to be considerably increased. In 1921 we found this content in abnormal milk (derived from diseased udders), and in colostrum to be very high. This is no doubt due to the occurrence in these kinds of milk of much protein, which is identic with, or related to the globulins of bloodserum, just as the other anomalies of the milk from cows with diseased

¹⁾ Milk containing streptococci has sometimes a high degree of acidity.

²⁾ Journ. Biol. Chem. 40. 335 (1919).

| No. (quarter). | Ordinary Acidity | Oxalate Acidity | p.H. | Sediment Trommsdorff (resp. number of leucocytes) | Chlorin mgrs. per 100 c.c. | Lactose % | Katalase figure | CaO mgrs. per 100 c.c. | Tryptophane (after precipitating with alum) mgrs. per 100 c.c. |
|--------------------|------------------|-----------------|-----------|---|----------------------------|-----------------|-----------------|------------------------|--|
| 381 (R.F.) | 2.5 | — | — | 0.35 % ¹⁾ | — | — | — | 120.2 | 110.6) |
| 382 > | 3.3 | — | — | 2.2 " ²⁾ | 298.4 | — | — | — | — } <i>after treatment of the</i> |
| 385 > | 5.3 | 1.3 | 6.98—7.06 | (mucus) ²⁾ | 280 | — ⁵⁾ | — | 196 | 300 } <i>udder with silver nitrate</i> |
| 387 > | 4.8 | 0 | 6.75—6.82 | 0.5 % ³⁾ | 153.6 | — | — | 101 | 90 } <i>streptococci occur</i> |
| 164 | 4.8 | 1.2 | 6.8—6.9 | ±1.5 c.c. | 290 | 1.3 | 6.9 | 188 | — } <i>" " Exam-</i> |
| 142 | 5.6 | 0.8 | 6.75—6.82 | 0.5 % ⁰⁾ | 149 | — | 3.5 | 179 | — } <i>ination</i> |
| 181 | 4.4 | 0.4 | 6.9—6.98 | 0.7 " | 220 | 3.2 | — | — | — } <i>absent</i> |
| 267 | 4.6 | 0.1 | 6.75—6.82 | 450 000 | 169 | — | 7 | — | — } <i>" " 1921.</i> |
| 343 (R.F.) | 7 | 2.3 | — | 0.35 % ⁰⁾ | 89.5 | 4.8 | — | 242.5 | — } <i>of "silvernitrate" cow before</i> |
| 337 > | 7.4 | — | — | 0.2 " | 107.7 | — | — | — | norm. } <i>treatment.</i> |
| 385 L.F. and L.B.) | 8.6 | 4.2 | 6.5—6.6 | — | — | — | — | — | — } <i>from other quarters of the</i> |
| 381 (L.F.) | 7 | — | — | 0.1 % ⁰⁾ ⁴⁾ | 84.3 | — | — | — | — } <i>"silvernitrate" cow; drawn</i> |

¹⁾ rather many leucocytes.

²⁾ full of leucocytes.

³⁾ few leucocytes, many cells with rounded nucleus.

⁴⁾ number of leucocytes normal.

⁵⁾ Milk drawn one day later contained 2.7 % lactose.

⁶⁾ Milk drawn one day later contained 348 mgrs. of tryptophan.

udders are connected with the transit of bloodplasma-components in abnormal milk. While 100 c.c. normal milk — after removal of casein and fat with the aid of potassium-alum contain according to our investigations about 14—20 mgrs. of tryptophane, as much as 348 mgrs. occurred in the milk-samples after the injection of silvernitrate, that is about twenty times more.

The determination of the tryptophane-content, easily executed by the colorimetical method of VON FÜRTH and NOBEL¹⁾, is no doubt one of the most accurate methods for examining the normality of milk.

The foregoing experiments tend to show that the anomalies characteristic of streptococci-containing milk, arise also from sterile inflammation of the udder-tissue, so that streptococci need not always be essential to the occurrence of similar anomalies. The question whether, in the case of streptococci-mastitis, these bacteria are very often only of secondary importance can of course not be answered on the basis of this investigation.

*From the Chemical Laboratory of the Veterinary
University of Utrecht.*

¹⁾ Biochem. Zts. 109. 103. (1920).

Microbiology. — “On *Bacillus polymyxa*”¹⁾. By Prof. M. W. BEIJERINCK and L. E. DEN DOOREN DE JONG.

(Communicated at the meeting of September 30, 1922).

If the species-conception is taken in a not too limited sense, the closely related, but not identic forms mentioned in Note 1, may be said to comprise the only known aërobic spore-forming bacterium-species, which causes fermentation in a sugar-containing medium. We call it *Bacillus polymyxa*.

It is rather generally spread in fertile soils; its properties are very characteristic and give rise to interesting experiments. The production of acetone first observed by SCHARDINGER, has in the later years drawn attention on this microbe, but the quantity formed is small and from malt or potatoes it does not amount to 1% of the weight. But the conditions for its formation are not yet well-known and might perhaps be greatly improved as to the quantity. Alcohol is also generated and to a somewhat greater amount than acetone. Besides, a little acetic- and formic acid seem to be produced. Particularly the secretion of the enzyme pectinase and of much slime by the chief variety is of interest.

¹⁾ The literature of this Bacterium and its nearest relations is to be found under: *Clostridium polymyxa* PRAZMOWSKI, *Granulobacter polymyxa* BEIJERINCK, *Bacillus macerans* SCHARDINGER and *Bacillus asterosporus* A. MEYER. — A. PRAZMOWSKI, Entwicklung und Fermentwirkung einiger Bacterien. Dissert. Leipzig 1880, p. 37. — TH. GRUBER, Identifizierung von *Clostridium Polymyxa* PRAZMOWSKI, Centralbl. f. Bakteriol. 2te Abt. Bd. 14, 1905, pag. 353. — F. SCHARDINGER, *Bacillus macerans*, Acetonbildender Rottebacillus, Centralbl. f. Bakt. 2te Abt. Bd. 14, 1905, pag. 772. Zur Biochemie von *B. macerans*. Centralbl. f. Bakt. 2te Abt. Bd. 19, 1907, p. 161. Kristallisierte Polysaccharide aus Stärke durch Mikroben. Centralbl. f. Bakt. 2te Abt. Bd. 22, 1909, p. 98 and Bd. 29, 1911, p. 189. — A. MEIJER und G. BREDEMANN, Variation und Stickstoffbindung durch *Bacillus asterosporus*. Centralbl. f. Bakteriol. 2te Abt. Bd. 22, 1909, p. 44.

The name *asterosporus* is derived from 9 or 10 rims on the exosporium of the oblong spores, which make the transversal section star-like. By abundant feeding, as on wort-gelatin, many rodlets change into narrow clostridia containing somewhat granulose, colored blue by iodine; so the species may also be called *Granulobacter polymyxa*.

Accumulation and occurrence.

Long ago the following experiment for the accumulation of this species was described ¹⁾.

Coarsely ground rye with some chalk and inoculated with fertile garden soil is mixed with water in a deep beaker to a thick solid paste, boiled during some seconds to kill the non-spore-formers and cultivated at 25° to 30° C. As the spores of *B. polymyxa* soon die at boiling, the heating must last but a short time. After a few days the surface is covered with a coherent film of *B. mesentericus* ²⁾ and other closely related species, while in the depth a butyric-acid fermentation takes place, usually simultaneously with butylic-alcohol- and polymyxa fermentation.

It is clear that this accumulation reposes essentially on a temporary anaërobiosis of *B. polymyxa*, which can also grow aërobic and so behaves like the alcohol yeast and the *Aërobacter-Coligroup* among the bacteria. The rye produces the sugar causing the fermentation, i.e. the source of energy, which makes the anaërobiosis possible so long as the "excitation oxygen" is still sufficiently present, albeit chemically non-demonstrable, whereas the want of "oxidation oxygen", which is required for aërobiosis in much larger quantity as source of energy, is temporarily excluded. PASTEUR'S statement: "la fermentation est la vie sans air" is evidently applicable to *B. polymyxa*.

By sowing out the fermenting matter from the depth on wort-agar, ordinarily already after few days the polymyxa colonies become visible as lumps of slime, together with the unavoidable flat spreading colonies of *B. mesentericus*.

This method can only produce those varieties of *B. polymyxa* which are able to resist a relatively high concentration of the food. Another accumulation method by which also forms adapted to a lower concentration of food are obtained is based on the aërobiosis of our bacterium.

After the observation had been made that flasks of boiled wort, not sufficiently sterilised, were not seldom spoiled at the low temperature of 15° C. by the development of *B. megatherium* and never by *B. mesentericus*, whose germs were certainly also present, the question

¹⁾ M. W. BEIJERINCK. De butylalcoholgisting en het butylferment. Academy of Sciences. Amsterdam 1893.

²⁾ This film may be colourless, brown, red, and even jet black according to the accidentally present varieties of *B. mesentericus*. The black form is rare and sometimes obtained by the "mesentericus experiment" with unwashed currants (boiling with chalk, cultivating at aëration at 30° to 40° C.).

arose: which are the aërobic spore-forming bacteria, which can develop at temperatures of 15° C. or lower and under favorable feeding conditions? We knew already that the obtaining of *B. megatherium* might give an answer to the question, for example in case the spores of this species were only present with those of *B. mesentericus*, but it seemed possible that free competition with the soil bacteria would exclude *B. megatherium* and that some other species could appear. The chief aim of the experiment was to exclude *B. mesentericus*, the common hay bacterium, which produces substances very noxious to other species, and this is to be reached by the low temperature, as the minimum for the growth of this species is at about 20° C. The simultaneous development of *B. megatherium* is of less importance as it is innocuous to other kinds. Of course we had to reckon with the butyric-acid and butylic fermentations, which may very well occur at 15° C, but strong aëration prevents them efficiently.

Although we could expect that the one or more species that were to develop under the chosen conditions would possess a higher temperature optimum than that used by us, we had not to fear a failure if only we cultivated above their minimum.

Knowing that the spores of some spore-formers, for example those of the butylic ferments, and thus perhaps, too, those of the species we sought for, could not or hardly resist boiling, the heating of the culture liquid containing the inoculation material and wanted for killing the non-spore forming species, was not continued much above 85° or 90° C. and only for a few seconds. We used flasks half filled with about 30 cM³ liquid, and in order not to miss somewhat rarer species, we inoculated with so much soil that on the bottom a layer of about 1 cM precipitated. This soil had previously been well-divided and freed from coarse particles. In such a thick layer a beginning of anaërobiosis is possible, but by shaking, butyric-acid or butylic fermentation may easily be stopped.

For food we used at first malt-wort, diluted to 2° to 5° BALLING, later broth-bouillon with 2% to 5% cane sugar, or glucose. Addition of chalk is not absolutely wanted for the success of the experiment but its presence proved favorable.

After we had ascertained with pure cultures of *B. polymyxa* that ammonium salts, nitrates and asparagine are very good sources of nitrogen, we also accumulated with sugars and ammonium sulphate, in a solution of tapwater 100, 2 to 5 % glucose or cane sugar, 0,05 % (NH₄)₂SO₄, and 0,02 % K₂ HPO₄ with some chalk. The execution of the experiment is as above, but after pasteurising,

the butyric-acid fermentation must be more completely excluded than when using broth-bouillon or malt-wort. For although the latter liquids contain an excellent nitrogen food for *B. polymyxa*, they are of less value for the butyric-acid ferments, for which the ammonium salts are preferable. Hence, in this case it is advisable to use a large ERLÉNMEIJERflask, as the great volume of soil which sinks to the bottom as inoculation material, can then be better aerated, by which butyric fermentation is prevented.

Although the growth is slow at the low temperature the liquid becomes distinctly turbid and in most cases this is accompanied with fermentation. This fermentation especially awakened our attention as we had expected an accumulation of *B. megatherium*, which causes no fermentation at all.

As the *Coli*- and *Aërogenes* fermentations had been prevented by the previous heating, the butyric-acid and butylic fermentations by the aëration, we now expected that the fermentation of *B. polymyxa* was obtained, and this was confirmed by the pure culture. The fermentation which is chiefly an alcoholic one, proves that our bacterium belongs to the facultative (temporary) anaërobes, and the examination of the gas showed that it is almost pure carbonic acid.

One of the most notable qualities of *B. polymyxa* is its secretion of pectinase, i. e. the enzyme by which some microbes dissolve the central lamellum of plant tissues, thereby disintegrating them into cells. Hence, *B. polymyxa* like *B. mesentericus* may under certain circumstances play a part in the retting of flax, although the real agent in this case is the anaërobic *B. pectinovorum*.

Beans, peas and other plant seeds, left to spontaneous corruption, may change into rich cultures of *B. polymyxa*, the cell-walls of cotyledons and of endosperm being easily attacked by pectinase, whereby the interior of the seeds is changed to a pulpos mass¹⁾. For the preparation of a pure culture this method is less recommendable than the two foregoing accumulations, on account of the numerous hay bacteria which thereby simultaneously develop; it is, however, a good way to get an initial material for the said accumulations themselves.

It seems to us that the generality of *B. polymyxa* in our surroundings and particularly in the soil should be explained by its pectinase secretion, which must give this species, in combination with its little want of air, a great advantage over the other saprophytes.

¹⁾ The enzyme seminase, which changes the endosperm of the Leguminosae (*Indigofera*, *Ceratonia*) into mannose, is perhaps identic with the pectinase of *B. polymyxa*.

The very common presence of *B. polymyxa* in the bark of the nodules of the Leguminosae is certainly also a direct consequence of its pectinase production. Its presence there is of so general occurrence, that it reminds more of symbiosis than of saprophytism. In the bacteroid tissue *B. polymyxa* is however completely absent.

Properties of the colonies.

The colonies on agar as well as those on gelatin are characteristic. On malt-wort gelatin they resemble at first thin, watery, sideways quickly extending, slowly liquefying layers, which by and by become deeper and cloudy by their strong growth. At length the gelatin is completely liquefied and then these cultures resemble those of common hay bacteria. On malt-wort agar there is a profuse production of slime, whence very distinct voluminous and wrinkled colonies appear. The slime attracts part of the pigment from the wort-agar thereby becoming brown-coloured, which gives a characteristic appearance to the colonies.

On glucose-kalium-phosphate-ammonium-phosphate-agar they become glass-like transparent, somewhat resembling glass globules, so peculiar that at estimating the number of germs in soil samples, they may directly be recognised and counted. Silica plates, saturated with food, also produce such drop-like colonies from soil. Some varieties form much less slime than others and this slime is either tough or soft.

Microscopically those with soft slime consist of much shorter rodlets. Hence, one is at first disposed to think of different species, but further research shows the similarity, which is the more convincing, when beside the natural varieties, the mutation phenomena in the pure cultures are studied. On cane-sugar-asparagine agar many colonies, at first quite homogeneous and soft, when getting older produce small, rather solid, transparent, secondary colonies which, after separation from their surrounding (which is not easy) prove to be constant. On malt-wort agar the variety with tough slime, when growing older produces extensive, flat secondary colonies, showing a hereditary loss of the factors for slime formation.

In liquid nutritive media the form resistant to high concentrations of the food gives remarkable cultures.

In a malt-wort of 10° BALLING at 30° they consist of excessively voluminous slime masses, forming after one or two weeks a thick, coherent, floating film, inflated by carbonic acid, whilst no hydrogen is detectable. Only in the anaërobic butylic fermentation something of the like may be observed but then much hydrogen is present.

Even the most slimy *Aërobacter* forms produce quite different submerged cultures equally dispersed through the solution.

The vigorously fermenting slime varieties of *B. polymyxa* produce acetone, probably after the formula



To the products of the anaërobic fermentation belong in particular aethyl alcohol, with traces of acetic acid and formic acid beside some other products, such as butylic glycol, in small quantities.

The less slimy varieties of *B. polymyxa* can only live in food of lower concentration and spread through the solution as *Bact. aërogenes*. Also in other respects there is similarity between *Bact. aërogenes* and *B. polymyxa*, so that there is cause to conclude to a real relationship. Still there is a great difference in so far as *aërogenes* can assimilate many organic salts, a power quite absent in *B. polymyxa*.

Nutrition.

For the investigation of the substances which can be assimilated by *B. polymyxa*, the auxanographic method is very convenient, particularly in relation to the carbohydrates, *B. polymyxa* being a real "sugar bacterium", which produces much cell-wall matter, which makes the auxanograms very distinct. In judging the latter it should be kept in view that, beside pectinase, *B. polymyxa* produces diastase, invertase and emulsin. In presence of sugar various nitrogen compounds are assimilable, of which, however, only nitrogen is taken up. We preferently used peptone, asparagine ureum, ammonium sulphate and saltpeter. Urease is not secreted; saltpeter is reduced to nitrite, not to nitrogen.

As in absence of sugar the carbon cannot be withdrawn from nitrogen compounds, such as peptone and asparagine, the growth, even on broth-bouillon-agar is but slight and is a criterion for the quantity of sugar present. Hence, if on this medium *B. polymyxa* is densely sown, only small, hardly visible colonies grow, consisting, however, of bacteria with abundant protoplasm and commonly motile. If on such a culture an assimilable carbohydrate is locally distributed, vigorous growth ensues, chiefly reposing on slime formation and a distinct auxanogram results, demarcated by the limit of diffusion of the substance. It is in fact the presence of a small amount of complete food at the starting of the experiment, together with excess of by themselves unassimilable nitrogen compounds, which enables the germs to change into small colonies, which

renders the further growth after addition of the carbohydrate very clear.

Most sugars and polyalcohols are readily assimilated by *B. polymyxa*. This we have ascertained for arabinose, glucose, levulose, mannose, galactose, cane-sugar, maltose, lactose, melibiose, raffinose, rhamnose, glycerin and mannite. On the other hand sorbite, dulcitol, erythritol and quercitol are not attacked. It is very notable that we did not find any organic salt assimilable by this organism.

The "sugar bacteria", to which *B. polymyxa* belongs, produce from carbohydrates much more visible cell-wall substance than protoplasm, if the carbohydrates exceed the nitrogen food and vice versa.

Hence, *B. polymyxa* may be found, as was observed above, in two microscopically greatly different conditions. At insufficient feeding with carbohydrates, for example on broth agar, it grows as highly motile rodlets, without slime wall; at copious feeding with carbohydrates, as immotile rodlets with a thick slime wall¹). This circumstance leads to the following experiment, only adapted to the variety of *B. polymyxa* which produces voluminous slime and grows strongly on malt-wort.

The bacterium densely sown on cane-sugar-kaliumphosphate-agar, containing but few nitrogen compounds, may form fairly large colonies consisting, however, almost entirely of the strongly swollen walls of the cells. By addition to the said medium of a few drops of complete food, for example a little broth or malt-wort, containing an excess of sugar, the slime walls grow surprisingly so that the plate covers with a relatively thick slime coat. This slime is built up of the sugars by one or more synthetically acting enzymes, that might be named "cyteses" and should be considered as the genes or factors of the cell-walls.

This slime has the remarkable property of being able to become itself a source of carbon food, but only at the moment when all the cane sugar and all the assimilable nitrogen compounds have been used. If at this time some such nitrogen compound as ammonium-sulphate or asparagin are brought on the slime coat of the plate, the bacteria begin anew to grow and produce new protoplasm from their own cell-walls. This leads to the peculiar consequence, that an auxanogram is produced sinking deep into the layer of slime. For, by the growth the bulk of the bacteria is diminished, because the walls, which chiefly consisted of water and were very voluminous, disappear and are replaced by living protoplasm. So the appearance of the auxa-

¹) Medici give to the cell-wall of bacteria the singular name of "capsule".

nograms is quite changed when compared with the original state, for by their intense increase the opaque bacteria produce an also opaque auxanogram, whilst the original slime was transparent like glass. This proves that, in this case at least, the biological function of the slime is that of a reserve food.

In this experiment cane sugar was the food for the slime production; as hereby inversion takes place, glucose and levulose are probably the building materials of the slime; that these sugars are assimilated was stated above, and that glucose may also serve for the described experiment we ascertained particularly.

The other sugars have not yet been extensively examined from this point of view, but it seems that all give the same result. This leads to the conclusion that probably no more than two or three factors or genes (endoenzymes) are active in the production of the cell-wall. The problem is evidently of theoretic interest and deserves nearer research.

The wall-substance, which certainly belongs to the cellulose group and therefore may be called cellulan, must have a high power of attraction for water, for else its surprising volume cannot be explained. Nevertheless its molecules cannot be very small as they cannot diffuse at all in water. It is not colored by jodine, nor is it attacked by diastase. But as *B. polymyxa* may use it as a food-substance, this species evidently can excrete an enzyme which dissolves it. It is not improbable that this enzyme is pectinase, but this question is not yet answered. Should this really prove to be true, then the other question arises whether the so-called pectose of the central lamellum of the tissues of the higher plants may not also be a cellulose modification, as it is also easily dissolved by pectinase. This view seems to be much more acceptable than the current hypothesis: the central lamellum should be the calcium salt of an acid, isomeric with arabin-acid.

On the great similarity between pectinase and the seminase of the seeds of the Leguminosae, I already earlier directed the attention. That the latter enzyme does not attack true cellulose is in accordance with the same property of pectinase.

SUMMARY.

With a not too limited species-conception *Clostridium polymyxa*, *Granulobacter polymyxa*, *Bacillus macerans*, and *Bacillus asterosporus* may be brought to one single species: *Bacillus polymyxa*.

It is the only hitherto known aërobic spore-former, which, in

neutral sugar-containing media excites fermentation and thereby proves able to live as a temporary anaërobie.

The chief products of the fermentation are carbonic acid and alcohol. At the aërobie life a little acetone results, evidently from oxidation of sugar.

Anaërobie accumulation is possible in rye paste at 30° C. after short boiling. Aërobie accumulation takes place in dilute malt-wort or broth with 2% to 5% sugar, after heating at 85° to 90° C. or short boiling with much garden soil and cultivation at 15° C. by which *B. mesentericus* is excluded, whose growth minimum is at about 20° C.

The general distribution of *B. polymyxa* in decayed plants and its occurrence in the bark of plant roots and of the nodules of the Leguminosae reposes on the production of pectinase, which dissolves the central lamellum of the cellular tissues.

B. polymyxa forms much slime from sugar, which must be considered as cell-wall substance. Without carbohydrates or polyalcohols its growth seems impossible, hence it develops but slightly on broth agar.

The slime may serve as reserve food.

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Mathematics. — “*On the Light Path in the General Theory of Relativity.*” By Prof. W. VAN DER WOUDE. (Communicated by Prof. H. A. LORENTZ.)

(Communicated at the meeting of September 30, 1922).

In EINSTEIN'S theory the path of a ray of light is found by putting the condition that it is a geodesic null line in the four-dimensional time space¹⁾. If accordingly we represent the line element of this time space by

$$ds^2 = \sum_{i,k} g_{ik} dx_i dx_k \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the light path satisfies equally the equations of the geodesic as those of the null line

$$ds = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As far as we know the remarkable relation existing between these differential equations, has not yet been pointed out. We shall prove that this may be expressed in the following way:

a geodesic having one element, i.e. one point with the tangent at that point, in common with a null line, is itself a null line.

In order to prove this we shall first give the equations of the geodesic a form different from the usual one (§ 1), as on account of (2) it is not desirable to take s for the independent variable. With a view to an application which we shall give later on, we take one of the coordinates of the time space for the independent variable.

We shall conclude by pointing out the (evident) physical meaning of the theorem.

§ 1. If the line element is represented by

$$ds^2 = \sum_{i,k} g_{ik} dx_i dx_k,$$

the equations of the geodesic are

$$\frac{d^2 x_\nu}{ds^2} + \sum_{\lambda, \mu} \left\{ \begin{matrix} \lambda \mu \\ \nu \end{matrix} \right\} \frac{dx_\lambda}{ds} \frac{dx_\mu}{ds} = 0 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

¹⁾ From this there follows for the statical field (g_{ik} independent of the time-coordinate x_0 and $g_{0l} = 0$ for $l \neq 0$) the principle of FERMAT for the minimum time of light in three dimensional space.

CHRISTOFFEL'S symbol $\left\{ \begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right\}$ has here the meaning :

$$\left\{ \begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right\} = \sum_{\tau} g^{\nu\tau} \left[\begin{matrix} \lambda & \mu \\ & \tau \end{matrix} \right],$$

where $g^{\nu\tau}$ is the algebraical minor of $g_{\nu\tau}$ in the g -determinant divided by this determinant, and

$$\left[\begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right] = \frac{1}{2} \left(\frac{\partial g_{\nu\lambda}}{\partial x_{\mu}} + \frac{\partial g_{\mu\nu}}{\partial x_{\lambda}} - \frac{\partial g_{\lambda\mu}}{\partial x_{\nu}} \right)$$

As independent variable we chose one of the coordinates, e.g. x_0 . In this case

$$\frac{dx_{\nu}}{ds} \times \frac{ds}{dx_0} = \frac{dx_{\nu}}{dx_0} ; \frac{d^2 x_{\nu}}{ds^2} \left(\frac{ds}{dx_0} \right)^2 + \frac{dx_{\nu}}{ds} \frac{d^2 s}{dx_0^2} = \frac{d^2 x_{\nu}}{dx_0^2} ; \dots \quad (4)$$

especially for $x_{\nu} = x_0$

$$\frac{d^2 x_0}{ds^2} \left(\frac{ds}{dx_0} \right)^2 = - \frac{dx_0}{ds} \frac{d^2 s}{dx_0^2} \dots \dots \dots (4')$$

If therefore we multiply the former of the equations

$$\frac{d^2 x_{\nu}}{ds^2} + \sum_{\lambda, \mu} \left\{ \begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right\} \frac{dx_{\lambda}}{ds} \frac{dx_{\mu}}{ds} = 0$$

$$\frac{d^2 x_0}{ds^2} + \sum_{\lambda, \mu} \left\{ \begin{matrix} \lambda & \mu \\ & 0 \end{matrix} \right\} \frac{dx_{\lambda}}{ds} \frac{dx_{\mu}}{ds} = 0$$

by $\left(\frac{ds}{dx_0} \right)^2$, the latter by $\left(\frac{ds}{dx_0} \right)^2 \frac{dx_{\nu}}{dx_0}$, we find after subtraction by the aid of (4) and (4')

$$\frac{d^2 x_{\nu}}{dx_0^2} + \sum_{\lambda, \mu} \left[\left\{ \begin{matrix} \lambda & \mu \\ & \nu \end{matrix} \right\} - \left\{ \begin{matrix} \lambda & \mu \\ & 0 \end{matrix} \right\} \frac{dx_{\nu}}{dx_0} \right] \frac{dx_{\lambda}}{dx_0} \frac{dx_{\mu}}{dx_0} = 0 \dots \dots (5)$$

These are the equations of the geodesic which we had in view. Taken as the equations of the geodesic of a two-dimensional space (a surface in the usual meaning), they give

$$\begin{aligned} \frac{d^2 v}{du^2} - \left\{ \begin{matrix} 2 & 2 \\ & 1 \end{matrix} \right\} \left(\frac{dv}{du} \right)^2 + \left(\left\{ \begin{matrix} 2 & 2 \\ & 2 \end{matrix} \right\} - 2 \left\{ \begin{matrix} 1 & 2 \\ & 1 \end{matrix} \right\} \right) \left(\frac{dv}{du} \right)^2 + \\ + \left(2 \left\{ \begin{matrix} 1 & 2 \\ & 1 \end{matrix} \right\} - \left\{ \begin{matrix} 1 & 1 \\ & 1 \end{matrix} \right\} \right) \frac{dv}{du} + \left\{ \begin{matrix} 1 & 1 \\ & 2 \end{matrix} \right\} = 0, \end{aligned}$$

a well known form, which is often taken as the starting point for the discussion of the properties of this line.

§ 2. We multiply (5) by $g_{\nu\rho} \frac{dx_\rho}{dx_\nu}$ and sum with respect to ν and ρ ; the equation thus found

$$\sum_{\nu,\rho} g_{\nu\rho} \left(\frac{d^2 x_\nu}{dx_0^2} + \sum_{\lambda,\mu,\nu,\rho} g_{\nu\rho} \left[\left\{ \begin{matrix} \lambda & \mu \\ \nu & \nu \end{matrix} \right\} - \left\{ \begin{matrix} \lambda & \mu \\ 0 & dx_0 \end{matrix} \right\} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \right] \frac{dx_\rho}{dx_0} \right) = 0 \quad (6)$$

may be reduced to a different form.

Let us consider the first term:

$$\sum_{\nu,\rho} g_{\nu\rho} \frac{d^2 x_\nu}{dx_0^2} \frac{dx_\rho}{dx_0};$$

As $g_{\nu\rho} = g_{\rho\nu}$ we may also write this

$$\frac{1}{2} \sum_{\nu,\rho} g_{\nu\rho} \left(\frac{d^2 x_\nu}{dx_0^2} \frac{dx_\rho}{dx_0} + \frac{d^2 x_\rho}{dx_0^2} \frac{dx_\nu}{dx_0} \right) = \frac{1}{2} \sum_{\nu,\rho} g_{\nu\rho} \frac{d}{dx_0} \left(\frac{dx_\nu}{dx_0} \frac{dx_\rho}{dx_0} \right).$$

In the second term

$$\sum_{\lambda,\mu,\nu,\rho} g_{\nu\rho} \left\{ \begin{matrix} \lambda & \mu \\ \nu & \nu \end{matrix} \right\} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \frac{dx_\rho}{dx_0}$$

we replace $\left\{ \begin{matrix} \lambda & \mu \\ \nu & \nu \end{matrix} \right\}$ by its expression between the square brackets and apply a reduction

$$\begin{aligned} \sum_{\lambda,\mu,\nu,\rho,\tau} g_{\nu\rho} g^{\nu\tau} \left[\begin{matrix} \lambda & \mu \\ \tau & \tau \end{matrix} \right] \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \frac{dx_\rho}{dx_0} &= \sum_{\lambda,\mu,\tau} \left(\left[\begin{matrix} \lambda & \mu \\ \tau & \tau \end{matrix} \right] \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \sum_{\nu,\rho} g^{\nu\tau} g_{\nu\rho} \frac{dx_\rho}{dx_0} \right) = \\ &= \sum_{\lambda,\mu,\tau} \left[\begin{matrix} \lambda & \mu \\ \tau & \tau \end{matrix} \right] \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \frac{dx_\tau}{dx_0}, \end{aligned}$$

as

$$\sum_{\nu} g^{\nu\tau} g_{\nu\rho} \begin{cases} \leq 1 & (\text{for } \rho = \tau) \\ \leq 0 & (\text{for } \rho \neq \tau) \end{cases}.$$

According to the meaning of the symbols [], we may replace the expression thus found by

$$\frac{1}{2} \sum_{\lambda,\mu,\tau} \frac{\partial g_{\lambda\mu}}{\partial x_\tau} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \frac{dx_\tau}{dx_0} = \frac{1}{2} \sum_{\lambda,\mu} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \frac{dg_{\lambda\mu}}{dx_0}.$$

The two former terms of (6) may therefore be combined to:

$$\frac{1}{2} \frac{d}{dx_0} \sum_{\lambda,\mu} g_{\lambda\mu} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} = \frac{1}{2} \frac{d}{dx_0} \left(\frac{ds}{dx_0} \right)^2.$$

We write the third term

$$\sum_{\lambda,\mu,\nu,\rho} g_{\nu\rho} \left\{ \begin{matrix} \lambda & \mu \\ \nu & \nu \end{matrix} \right\} \frac{dx_\nu}{dx_0} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \frac{dx_\rho}{dx_0}$$

as

$$\sum_{\lambda, \rho} \left(g_{\nu \rho} \frac{dx_\nu}{dx_0} \frac{dx_\rho}{dx_0} \sum_{\lambda, \mu} \begin{Bmatrix} \lambda & \mu \\ & 0 \end{Bmatrix} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} \right) = \left(\frac{ds}{dx_0} \right)^2 \sum_{\lambda, \mu} \begin{Bmatrix} \lambda & \mu \\ & 0 \end{Bmatrix} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0},$$

so that (6) is transformed into

$$\frac{1}{2} \frac{d}{dx_0} \left(\frac{ds}{dx_0} \right)^2 + \left(\frac{ds}{dx_0} \right)^2 \sum_{\lambda, \nu} \begin{Bmatrix} \lambda & \mu \\ & 0 \end{Bmatrix} \frac{dx_\lambda}{dx_0} \frac{dx_\nu}{dx_0} = 0 \quad \dots \quad (7)$$

§ 3. Let us now define a line in time space by

$$x_i = \varphi_i(x_0),$$

where we require of the functions φ :

1. that the line defined in this way satisfy the equations of the geodesic;

2. that in a definite point A

$$\left(\frac{ds}{dx_0} \right)_A^2 = \sum_{i,k} \left(g_{ik} \frac{dx_i}{dx_0} \frac{dx_k}{dx_0} \right)_A = 0.$$

Of course we also suppose that the coordinates x_i are defined as uniform continuous functions of x_0 and that also g_{ik} and its derivatives are uniform continuous functions of the coordinates, at least in the region in consideration.

We have in this way taken care that the line defined by (8) is a geodesic and has a null element in A . As it is a geodesic each of its points satisfies (7); each x_i being a function of x_0 , we may conclude that

$$\frac{d}{dx_0} \left(\frac{ds}{dx_0} \right)^2 - \left(\frac{ds}{dx_0} \right)^2 \Phi(x_0) = 0,$$

where Φ is a uniform continuous function of x_0 .

Hence, along each geodesic

$$\left(\frac{ds}{dx_0} \right)_P^2 = \left(\frac{ds}{dx_0} \right)_A^2 e^{\int_{\alpha_0}^{\rho_0} \Phi(x_0) dx_0}; \quad \dots \quad (8)$$

by α_0 and ρ_0 we understand the values which x_0 assumes at the starting point A and an arbitrary point P of the line.

However, we have also made the assumption that the geodesic in consideration has a null element in A . Accordingly here

$$\left(\frac{ds}{dx_0} \right)_A^2 = 0.$$

On the other hand there follows from (8) that along this line always

$$\left(\frac{ds}{dx_0} \right)^2 = 0,$$

in other words that the line in consideration is a geodesic null line, which was to be proved.

§ 4. Let x_0 be the time coordinate. In three-dimensional space in a point A an arbitrary direction is defined by giving definite ratios to $\frac{dx_l}{dx_0}$ ($l = 1, 2, 3$). If inversely we assume these ratios as given, we can give such values to $\frac{dx_l}{dx_0}$ that the condition

$$\left(\frac{ds}{dx_0}\right)^2 \equiv \sum_{\lambda, \mu} g_{\lambda\mu} \frac{dx_\lambda}{dx_0} \frac{dx_\mu}{dx_0} = 0 \quad (\lambda, \mu = 0, 1, 2, 3).$$

is satisfied.

The theorem which we have proved, has therefore the meaning:
In three-dimensional space there passes a ray of light at any moment through any point in any direction.

Physics. — “*Calculations of the effective permeability and dielectric constant of a powder.*” By G. BREIT, National Research Fellow U.S.A. (Supplement N°. 46 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated at the meeting of October 28, 1922).

Introductory.

The pure samples of some rare substances are available only in powdered form and show particularly interesting magnetic properties. For this reason it is desirable to know the relation between the measured and the true permeability of a powdered substance.

If the susceptibility is small the effects of the demagnetizing field are negligible and the magnetization of any individual particle of the powder is the same as it would be if the particle were part of a solid block. Supposing that the particles are crystalline, the measured specific susceptibility is the mean specific susceptibility of a crystal provided in taking the mean equal weights are given to all orientations of the crystal.

In the case of gadolinium sulphate at 2° K. the magnetization is considerable and the above approximation does not suffice. This fact has been realized by Prof. H. KAMERLINGH ONNES and a correction has been made by him¹). Prof. KAMERLINGH ONNES expressed his desire to the author to see a more accurate correction. This forms the subject of the following pages.

Approximations and statement of problem.

In view of the random distribution of the principal directions of the individual crystalline particles the difference between susceptibilities in different directions will be neglected. This probably introduces an error in the calculations which however is likely to be small.

It will be supposed that the applied field is so small that the magnetization is proportional to the field. Some of the results of the calculation are independent of this assumption as will be brought out later.

¹) Leiden Comm. Suppl. N°. 44a p. 10.

For convenience of notation the electrostatic problem of a powdered dielectric in an electric field will be treated. The results are translated into the magnetic case by substituting the permeability μ for the dielectric constant ϵ .

Our problem is to calculate the effective dielectric constant of a powder under the above assumptions as to the smallness of the field and the random distribution of the axes when the density of packing of the powder and the dielectric constant of the material of the powder are known.

Definition of "effective dielectric constant".

Let us consider a portion of the powder which contains many particles and let us take the mean electric intensity and the mean electric displacement throughout this portion. (The mean being taken with respect to volume). We define: "effective dielectric constant" =
$$= 4\pi \frac{\text{mean electric displacement}}{\text{mean electric intensity}}.$$

We presuppose that this definition is unique which implies that the powder is sufficiently fine for otherwise it is not possible to include a sufficient number of particles without making the portion so large that the field would vary in it (from point to point) if the powder were replaced by a solid.

Let us draw a spherical surface inside the powder. According to the well known treatment of polarized media the electric intensity inside the sphere is equal to the electric intensity due to charges inside the sphere plus the intensity due to charges of polarization on the surface of the sphere and plus the intensity due to charges of polarization on the outer surface of the powder as well as that due to charges outside and inside the powder. This means that the electric intensity

$$E = E_i + E_p + E_o$$

where

E_i = effect of charges inside the sphere

E_p = effect of charges of polarization on the surface of the sphere

E_o = effect of charges of polarization on the outer surface of the powder + external field

where "external field" = field due to all real charges and the charges of polarization not belonging to the powder.

Since each individual particle is uncharged E_i is obtained by summing the fields due to charges of polarization on the surfaces of the particles inside the sphere.

If \bar{E}_0 should denote the average value of E_0 throughout the sphere we have with a good approximation $\bar{E}_0 = \bar{E}$ because the usual treatment of polarized media may be applied to \bar{E} and the result is E_0 if the powder is fine.

Let a certain volume be occupied by the powder and put in an external field \mathfrak{E} . Then $E_0 \neq \mathfrak{E}$ on account of the charges of polarization on the outer surface of the volume. It is for this fact that the correction has been made by Prof. H. KAMERLINGH ONNES. We shall suppose in what follows that this or an equivalent correction is made in the final interpretation of the experiment. In order to make such a correction however one must first obtain the effective dielectric constant and then operate with this constant just as one would in the case of a homogeneous medium. Thus e.g. it may be shown¹⁾ that the force on a sphere of radius a placed in a field of force given by $E_0 + Bz$ parallel to the OZ axis of a rectangular system of coördinates having its origin at the centre of the sphere and $-\frac{B\rho}{2}$ along the radius ρ perpendicular to the axis of z is $F = a^3 \frac{\epsilon - 1}{\epsilon + 2} BE_0$ where E_0 , B are constants and ϵ is the dielectric constant. Hence

$$\epsilon = \frac{2 F / a^3 B E_0 + 1}{1 - F / a^3 B E_0}$$

Preliminary approximate solutions.

(a) *A space lattice of spheres.*

Consider a space lattice of spheres the density of packing being not too great. We can get very easily an approximate solution for this case. Let us suppose that each sphere has its boundary removed so far from the surface of the adjacent spheres that the field acting

¹⁾ Using equation (6) (to be derived presently) we find that the density of the fictitious distribution of charge is (using polar coördinates with OZ as axis)

$$\sigma_i = \frac{1}{4\pi} (E_{in_2} - E_{in_1}) = \frac{1}{4\pi} \left[\frac{3(\epsilon - 1)}{\epsilon + 2} E_0 P_1(\cos \theta) + \frac{5(\epsilon - 1)}{2\epsilon + 3} B a P_2(\cos \theta) \right].$$

Hence the force

$$F = \int_{\cos \theta = -1}^{+1} \frac{a^3}{2} [E_0 + B a P_1(\cos \theta)] \left[\frac{3(\epsilon - 1)}{\epsilon + 2} E_0 P_1(\cos \theta) + \frac{5(\epsilon - 1)}{2\epsilon + 3} B a P_2(\cos \theta) \right] d(\cos \theta) = a^3 \frac{\epsilon - 1}{\epsilon + 2} E_0 B.$$

on it may be considered as uniform. Then the sphere is uniformly polarized, the polarization being $\frac{3}{4\pi} \frac{\epsilon_0 - 1}{\epsilon_0 + 2} F$, where ϵ_0 is the dielectric constant of the sphere and F is the uniform field acting on the sphere. If q should denote the fraction of the volume of the lattice which is occupied by the spheres themselves, the average polarization is

$$P = \frac{3q}{4\pi} \frac{\epsilon_0 - 1}{\epsilon_0 + 2} F.$$

Since now the effect of a uniformly polarized sphere at points outside the sphere is equivalent to the effect of a doublet at the centre of the sphere the contribution to F of the particles of powder situated inside the large spherical hole vanishes by a well known reasoning of LORENTZ¹⁾ and his result for F' applies here so that

$$F = E + \frac{4\pi}{3} P = E + q \frac{\epsilon_0 - 1}{\epsilon_0 + 2} F$$

i.e.

$$F' = \frac{E}{1 - q \frac{\epsilon_0 - 1}{\epsilon_0 + 2}}$$

and

$$P = \frac{3q}{4\pi} \frac{E}{\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - q} = \frac{\epsilon - 1}{4\pi} E$$

where ϵ is the effective dielectric constant.

Thus

$$\frac{\epsilon - 1}{q(\epsilon_0 - 1)} = \frac{1}{\frac{\epsilon_0 + 2}{3} - \frac{q}{3}(\epsilon_0 - 1)} \dots \dots \dots (1)$$

and letting

$$p + q = 1$$

$$\epsilon_0 = 1 + d \dots \dots \dots (1A)$$

we have

$$\frac{\epsilon - 1}{q(\epsilon_0 - 1)} = \frac{1}{1 + \frac{pd}{3}} \dots \dots \dots (1')$$

Thus the effective susceptibility of a powder is not proportional

¹⁾ H. A. LORENTZ, Theory of Electrons, p. 308

to the density of packing but should be corrected by the factor $\frac{1}{1+p\delta/3}$.

It is worth noting that (1) may be written as

$$\frac{\epsilon-1}{\epsilon+2} = q \frac{\epsilon_0-1}{\epsilon_0+2} \dots \dots \dots (1'')$$

which means that if the powder is moulded in a sphere then the force on that sphere is a q^{th} part of the force which would be exerted on a solid sphere of the same radius. In other words each individual particle of the powder may be considered as acted on only by the external force. (I have seen a very direct and simple proof of this fact from Prof. EHRENFEST).

We see therefore that to within the approximations made so far the factor $\frac{1}{1 + \frac{4\pi\sigma d}{3H}}$ used by Prof. H. KAMERLINGH ONNES should be

used with the value of the density in the solid — not the powdered form.

(b) *A space lattice of spherical holes*¹⁾.

The case considered above may be expected to give a good approximation if the powder is packed loosely. If it is packed closely a better approximation must be expected from a space lattice of holes.

It is not necessary to treat this case independently because use can be made of formula (1) if it is remembered that in (1) ϵ is the ratio of the effective dielectric constant to the dielectric constant of the space between the spheres of the lattice. Denoting by q as before the proportion of the volume occupied by the substance (i.e. the ratio to the total volume of total volume minus the volume of the holes) and leaving (1A) unchanged we arrive at

$$\frac{\epsilon-1}{q(\epsilon_0-1)} = \frac{1}{1 + \frac{p\delta}{3+2\delta}} \dots \dots \dots (2)$$

which may be also shown to be equivalent to

$$\frac{\epsilon-1}{\epsilon_0-1} = \frac{1}{1 + \frac{3\epsilon_0 p}{1+2\epsilon_0 q}} \dots \dots \dots (2')$$

¹⁾ The possibilities of this case have been pointed out to me by Prof. H. KAMERLINGH ONNES and Dr. H. R. WOLTJER.

From either of these formulas we find

$$\frac{\epsilon - 1}{\epsilon + 2} = q \frac{\epsilon_0 - 1}{\epsilon_0 + 2 - \frac{2p\delta^2}{3 + 2\delta}} \dots \dots \dots (2'')$$

This formula is analogous to (1'') in (a) and shows that to within the first power of δ the force on a sphere having spherical holes in it is the same as if the sphere were moulded into a smaller sphere without holes. Thus the conclusions drawn in (a) for the correction factor

$$1 + \frac{1}{3} \frac{4\pi \sigma d}{H}$$

(c) *Laminary structure of powder the directions of the laminae being distributed statistically. (See fig. 1).*

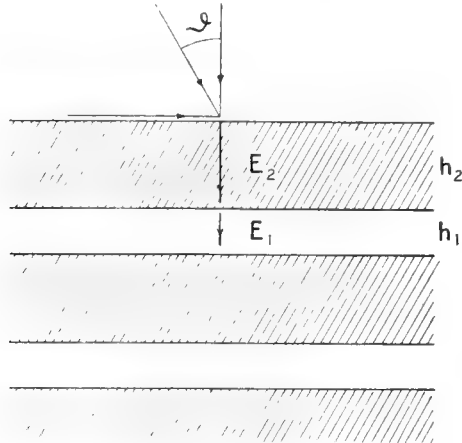


Fig. 1.

The electric intensity may be resolved into two components normal and parallel to the laminae respectively.

(I) Normal component.

Letting $E_1, E_2, h_1, h_2, \epsilon_1, \epsilon_2$ be respectively the normal components of the field intensity, the thicknesses, and the dielectric constants of the interspaces between the laminae and the laminae themselves we have:

$$\frac{E_1}{\epsilon_1 - 1} = \frac{E_2}{\epsilon_2 - 1} = \frac{h_1 E_1 + h_2 E_2}{h_1 \epsilon_1 - 1 + h_2 \epsilon_2 - 1}$$

Writing

$$h_1 E_1 + h_2 E_2 = (h_1 + h_2) \bar{E}$$

and letting

$$\frac{\bar{E}}{\epsilon_n^{-1}} = \frac{E_1}{\epsilon_1^{-1}}$$

we obtain

$$\epsilon_n = \frac{h_1 + h_2}{h_1 \epsilon_1^{-1} + h_2 \epsilon_2^{-1}} = \frac{1}{p + q \epsilon_0^{-1}}$$

having let

$$\epsilon_1 = 1, \epsilon_2 = \epsilon_0, \frac{h_2}{h_1 + h_2} = q, \frac{h_1}{h_1 + h_2} = p.$$

This number ϵ_n is the effective dielectric constant for the component normal to the laminae.

(II) Parallel component.

For this it is clear that the effective dielectric constant is

$$\epsilon_p = \frac{h_1 \epsilon_1 + h_2 \epsilon_2}{h_1 + h_2} = p + q \epsilon_0$$

(III) Both components present.

The electric displacement is $\frac{E}{4\pi} (\epsilon_n \cos \vartheta, \epsilon_p \sin \vartheta)$ where ϑ is the angle made by the mean electric intensity with the normal to the laminae. Since the directions of the normals to the laminae are entirely arbitrary with respect to the direction of the mean electric intensity, the component of the electric displacement perpendicular to the mean electric intensity is distributed at random. The only component to be considered is then that parallel to the mean electric intensity which is $\frac{E}{4\pi} (\epsilon_n \cos^2 \vartheta + \epsilon_p \sin^2 \vartheta)$. The effective dielectric constant is

$$\epsilon = \epsilon_n \overline{\cos^2 \vartheta} + \epsilon_p \overline{\sin^2 \vartheta} = \frac{\epsilon_n + 2 \epsilon_p}{3}$$

Hence we get

$$\frac{\epsilon - 1}{q(\epsilon_0 - 1)} = \frac{1 + \frac{2}{3} p \sigma}{1 + p \sigma} \dots \dots \dots (3)$$

To within the first power of σ this is the same as (2) or (1') so that in this case the conclusions drawn as to a force on a sphere are still valid. Rewriting (3) in the form

$$\frac{\epsilon - 1}{q(\epsilon_0 - 1)} = \frac{1}{1 + \frac{p \sigma}{3 + 2 p \sigma}} \dots \dots \dots (3')$$

it becomes apparent that the value of ϵ obtained from (3') lies between the values obtained from (1') and (2).

Variable susceptibility.

To within the approximations made so far the case of variable susceptibility offers no difficulty. Thus in the case (a) it was assumed that the field acting on each particle of the powder is uniform. Whether the susceptibility of this particle depends on the field or not its polarization is uniform and is such that the electric intensity E inside the particle is

$$E = \frac{3}{\epsilon_0(E) + 2} F$$

where F is the intensity of the field acting on the particle and $\epsilon_0(E)$ is the value of the dielectric constant of the material of the particle corresponding to E . If the mean field is \bar{E} , $F = \bar{E} + \frac{4\pi}{3} P$

and $P = q \frac{\epsilon_0(E) - 1}{4\pi} E$. Hence E and ϵ_0 are the result of solving the simultaneous equations

$$\left(\epsilon_0 + \frac{3}{p} - 1 \right) E = \frac{3}{p} \bar{E} \left\{ \right.$$

$$\epsilon_0 = \epsilon_0(E)$$

The solution may be obtained graphically or otherwise.

In the calculations that follow the correction for variable susceptibility is more complex and will not be considered.

The distribution of potential in a rectangular space lattice of dielectric spheres.

In order to investigate the errors involved in the approximations we shall look for an exact solution in the case of a space lattice of dielectric spheres. The following notation will be employed:

h = distance between centres of adjacent spheres.

ϵ_0 = dielectric constant of the material of the spheres.

(r, ϑ, φ) = polar coördinates of a point referred to centre of sphere placed at the origin. The polar axis is chosen along one of the rectangular axes of the lattice.

$(r_1, \vartheta_1, \varphi_1)$ = polar coördinates of a point referred to centre of sphere whose Cartesian coördinates are:

(x_1, y_1, z_1) and whose polar coördinates are:

(R_1, Θ_1, Φ_1) .

The radius of each sphere is taken to be 1. The mean field is also supposed to be 1 and directed along the polar axis.

Polarization of single sphere in external field.

Before proceeding with the solution of the problem it will be convenient to derive an expression for the state of polarization of a dielectric sphere placed in a known external field. Charges of polarization are induced. If the electric intensity due to these charges be E_i and if the impressed electric intensity be E_e , the total intensity is $E = E_e + E_i$. Let us suppose that E_i may be derived from a potential

$$V = \sum_{n,m} \frac{A_n^m P_n^m(\cos \vartheta) \cos m\varphi}{r^{n+1}} \dots \dots \dots (4)$$

outside the sphere. Then it must be derivable from

$$V = \sum_{n,m} A_n^m r^n P_n^m(\cos \vartheta) \cos m\varphi \dots \dots \dots (5)$$

inside the sphere since the potential is continuous at the surface. Denoting the components along the outward drawn normal by the suffix n and referring to the state just inside the sphere by n_1 and to the state just outside by n_2 we have the boundary condition

$$\epsilon_0 (E_{en} + E_{in_1}) = E_{en} + E_{in_2}$$

or

$$(\epsilon_0 - 1) E_{en} = E_{in_2} - \epsilon_0 E_{in_1}$$

Using (4) and (5)

$$(\epsilon_0 - 1) E_{en} = \sum_{n,m} (n\epsilon_0 + n + 1) A_n^m P_n^m(\cos \vartheta) \cos m\varphi \dots \dots (6)$$

Thus if E_{en} can be expanded in a series of surface harmonics the coefficients A_n^m may be determined from (6) and hence the state of polarization of the sphere may be obtained.

Derivation of expansion for E_{en} .

In order to solve the problem it will be sufficient to express E_{en} in terms of A_n^m and substitute the result in (6).

The average polarization of the medium being $\frac{A_1^0}{h^3}$ we have

$$E_{en} = \left(1 + \frac{4\pi A_1^0}{3 h^3} \right) \cos \vartheta - \frac{\partial}{\partial r} \left(\sum' \sum_{n,m} \frac{A_n^m P_n^m(\cos \vartheta_1) \cos m\varphi_1}{r_1^{n+1}} \right)_{r=1}$$

the first summation being extended over all the spheres inside a large sphere having its centre at the origin, the dielectric sphere situated at the origin being omitted from the summation as indicated by the accent. Using the notation:

$$D_{(c)}^m = \frac{\partial^{n-m}}{\partial z^{n-m}} D_{(c)}^m$$

$$D_c^m = \frac{\partial^m}{\partial \xi^m} + \frac{\partial^m}{\partial \eta^m}$$

$$\xi = x + i y, \quad \eta = x - i y$$

and letting

$$b_0 = 1; \quad b_1, b_2, \dots = \frac{1}{2}$$

it may be shown that [see appendix formula (1A)]

$$\frac{\cos m \varphi_1 P_n^m(\cos \vartheta_1)}{r_1^{n+1}} = \frac{(-)^n 2^m b_m}{(n-m)!} D_{(c)}^m \left(\frac{1}{r_1} \right) \dots \dots (7)$$

the differentiation being performed with respect to the end point of the vector r_1 i.e. with respect to (r, ϑ, φ) . Thus

$$E_{en} = \left(1 + \frac{4\pi A_1^0}{3 h^3} \right) \cos \vartheta - \frac{\partial}{\partial r} \left(\sum_{m,n=1,\dots} \frac{(-)^n 2^m b_m A_n^m}{(n-m)!} D_{(c)}^m \sum_1' \left(\frac{1}{r_1} - \frac{1}{R_1} \right) \right)_{r=1}$$

where $\frac{1}{R_1}$ has been subtracted from $\frac{1}{r_1}$ so as to secure absolute convergence of expansions that follow. Now

$$\frac{1}{r_1} - \frac{1}{R_1} = \sum_{m=0,\dots,n} \frac{r^n}{R_1^{n+1}} \frac{(n-m)!}{b_m(n+m)!} P_n^m(\cos \vartheta) P_n^m(\cos \Theta_1) \cos m(\varphi - \Phi_1).$$

When this is summed with respect to R_1, Θ_1, Φ_1 terms in $\sin m \Phi_1$ and all terms with an odd m drop out. Hence

$$E_{en} = \left(1 + \frac{4\pi A_1^0}{3 h^3} \right) \cos \vartheta - \frac{\partial}{\partial r} \left(\sum_{m,n} \frac{(-)^n 2^m b_m A_n^m}{(n-m)!} D_{(c)}^m \sum_{\nu,\mu} r^\nu P_\nu^\mu(\cos \vartheta) \cos \mu \varphi \frac{S_\nu^\mu}{b_\mu} \right)_{r=1}$$

where

$$S_\nu^\mu = \sum' \frac{(\nu-\mu)! P_\nu^\mu(\cos \Theta_1) \cos \mu \Phi_1}{(\nu+\mu)! R_1^{\nu+1}} \dots \dots (8)$$

Now it may be shown that [see Appendix formula (2A)]

$$D_{(c)}^m \left(\frac{r^\nu P_\nu^\mu(\cos \vartheta) \cos \mu \varphi}{b_\mu} \right) = \frac{(-)^m}{2^m} \frac{(r+\mu)!}{(\nu+\mu-n+m)!} \frac{r^{\nu-n} P_{\nu-n}^{\mu+m}(\cos \vartheta) \cos(m+\mu) \varphi}{b_{m+\mu}}$$

which when substituted into the expression for E_{en} just found gives:

$$E_{en} = \left(1 + \frac{4\pi A_1^0}{3 h^3} \right) P_1(\cos \vartheta) - \left. \begin{aligned} & - \sum (-)^{n+m} \frac{b_m}{b_{m+\mu}} \frac{(\nu+\mu)! (\nu-n) A_n^m S_\nu^{\mu+m} P_{\nu-n}^{\mu+m}(\cos \vartheta) \cos(m+\mu) \varphi}{(n-m)! (\nu+\mu-n+m)!} = \\ & = \sum_{n,m} \frac{(n\varepsilon_0 + n + 1) A_n^m P_n^m(\cos \vartheta) \cos m \varphi}{\varepsilon_0 - 1} \end{aligned} \right\} \dots (9)$$

in virtue of (6). Equating coefficients of P_1 we have

$$\left(\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - \frac{4\pi}{3h^3}\right) A_1^0 = 1 + 4A_3^0 S_4^0 + 6A_5^0 S_6^0 + \dots \quad (10)$$

where use is made of the fact that $S_2^0 = \sum' \frac{\frac{3}{2} \cos^2 \Theta_1 - \frac{1}{2}}{R_1^3} = 0$. In order to obtain $A_1^{(0)}$ we are thus in need of A_3^0, A_5^0 , etc. For these it follows from (9) that

$$\frac{[(2s + 1)\epsilon_0 + 2s + 2] A_{2s+1}}{\epsilon_0 - 1} = \sum_{p=0,1,\dots}^{\infty} \frac{(2s + 2p + 2)! S_{2s+2p+2}}{(2s)! (2p + 1)!} A_{2p+1} \quad (s = 1, 2, 3, \dots)$$

the upper subscript being dropped for the present. Writing

$$\left. \begin{aligned} \beta_s &= \frac{\epsilon_0 - 1}{\epsilon_0 + \frac{2s + 2}{2s + 1}}; \quad \alpha_s = \frac{A_{2s+1}}{A_1} \quad ; \quad (s, p) = \frac{(2s + 2p + 2)!}{(2s + 1)! (2p + 1)!} \\ S_{2p+2s+2} &= \sigma_{p+s} \end{aligned} \right\} \quad (11)$$

we have

$$\alpha_s = \beta_s \sum_{p=0}^{\infty} (s, p) \sigma_{p+s} \alpha_p, \quad (s = 1, 2, 3, \dots) \quad (12)$$

or

$$\alpha_s = \beta_s (s, 0) \sigma_s + \beta_s \sum_{p=1}^{\infty} (s, p) \sigma_{p+s} \alpha_p \quad (12')$$

Substituting for α_p on the right hand side the expression which follows for it from (12') and proceeding in this manner indefinitely we obtain purely symbolically on changing suffixes:

$$\begin{aligned} \alpha_s &= \beta_s (s, 0) \sigma_s + \sum_{s_1=1}^{\infty} \beta_s \beta_{s_1} (s, s_1) (s_1, 0) \sigma_{s+s_1, s_1} + \\ &+ \sum_{s_1, s_2=1}^{\infty} \beta_s \beta_{s_1} \beta_{s_2} (s, s_1) (s_1, s_2) (s_2, 0) \sigma_{s+s_1, s_1+s_2, s_2} + \dots \\ &+ \sum_{s_1, \dots, s_p=1}^{\infty} \beta_s \beta_{s_1} \dots \beta_{s_p} (s, s_1) (s_1, s_2) \dots (s_{p-1}, s_p) (s_p, 0) \sigma_{s+s_1, s_1+s_2, \dots, s_{p-1}+s_p, s_p} + \dots \end{aligned}$$

where

$$\sigma_{x,y,z,\dots} = \sigma_x \sigma_y \sigma_z \dots \quad (13)$$

If the spacing of the lattice is large in comparison with the diameter of each sphere this expansion may be expected to converge rapidly. As a first approximation the first term will suffice giving

$$\alpha_s = (2s + 2) \beta_s \sigma_s \quad (13')$$

Using (10) and (11) we have for the average polarization $P = A_1 h^{-3}$ and the effective dielectric constant ϵ

$$\epsilon - 1 = 4\pi P = \frac{3q}{\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - q - \sum_1^{\infty} (2s + 2) \alpha_s \sigma_s} \quad . . . (14)$$

where $q = \frac{4\pi}{3} h^{-3}$ and denotes as before the proportion of the total space occupied by the material of dielectric constant ϵ_s .

So far we have considered the field only in the direction of one of the axes of the lattice. If the lattice is rectangular and not cubical the quantities σ_s may be different for the three principal directions. In the case of a cubical lattice however they are the same. Since all the relations of the problem are linear the effective dielectric constant in a cubical lattice is independent of the direction of the field and may be thus justly compared with the effective dielectric constant of a powder.

If the first approximation (13') is substituted for α_s into (14) the approximate formula

$$\epsilon - 1 = \frac{3q}{\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - q - \sum_1^{\infty} (2s + 2)^2 \beta_s \sigma_s^2} \quad (14')$$

is obtained. In the summation of this formula the density of packing enters through the quantities σ_s and the intensity of polarization comes in through β_s . The quantity $\epsilon_0 - 1$ occurs in these to the first power. If the more accurate formula (13) were used higher powers of $\epsilon_0 - 1$ would come in. Hence if the density of packing is kept constant and if deviations from the simple formula (1'') just become apparent due to an increase in ϵ_0 formula (14') is the proper one to use. On using (11) it may be simplified to

$$\epsilon - 1 = \frac{3q}{\frac{\epsilon_0 + 2}{\epsilon_0 - 1} - q - (\epsilon_0 - 1) \sum_1^{\infty} \frac{2s + 1}{4s + 3} (2s + 2)^2 \bar{\sigma}_s^2 \left(\frac{6q}{\pi}\right)^{\frac{4s}{3} + 2}} \quad (14'')$$

where $\bar{\sigma}_s$ is the value of σ_s for $q = \frac{\pi}{6}$ which is the maximum possible q for the lattice. The quantities $\bar{\sigma}_s$ are rapidly diminishing as s increases. Thus we find

$$\frac{3}{7} (4\bar{\sigma}_1)^2 = 0.0646, \quad \frac{5}{11} (6\bar{\sigma}_2)^2 = 0.00032.$$

Writing

$$q' = \sum_1^{\infty} \frac{2s + 1}{4s + 3} (2s + 2)^2 \bar{\sigma}_s^2 \left(\frac{6q}{\pi}\right)^{\frac{4s}{3} + 2} \quad (15)$$

we get on neglecting terms of higher order than the second in $\epsilon_0 - 1$

$$\frac{\epsilon - 1}{\epsilon + 2} = q \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \left[1 + \frac{(\epsilon_0 - 1)^2}{3} q' \right] \dots \dots \dots (16)$$

Thus owing to the interaction among the particles of the powder the force on a ball made of the powder can no longer be considered as the sum of the forces on the individual particles independently. The increase of the force to within terms in $(\epsilon_0 - 1)^2$ is given by the factor $1 + \frac{(\epsilon_0 - 1)^2}{3} q'$. For the maximum possible value of q for the model considered $q' = 0.065$ and the correction factor becomes $1 + \frac{(\epsilon_0 - 1)^2}{46}$. If the quantity $\frac{4\pi \sigma d}{3H}$ of Suppl. N^o. 44a is 0.09 for gadolinium sulphate at 2° K. then since d was taken as $\frac{3}{4}$ of the actual density the quantity $\epsilon_0 - 1$ becomes 0.36 and the correction factor is 1.0028. Thus the effect discussed must be taken into account if the measurements of the force are made to within 0.3%. If such a correction is made it should be also borne in mind that even the simple formula (1'') involves terms of the second order in the apparent $(\epsilon - 1)$ if it is solved for ϵ_0 as may be seen in the following way.

For small values of $\epsilon_0 - 1$ we have $q(\epsilon_0 - 1) = \kappa F'$ where F' is the force and κ is a constant of the apparatus. For larger values of $\epsilon - 1$ this is not true but it is convenient to call the quantity $\epsilon_a - 1$ defined by the above equation: "the apparent $\epsilon - 1$ ". If the sample is spherical and if the powder may be considered as the cubical lattice just discussed

$$q \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \frac{1}{1 - \frac{(\epsilon_0 - 1)^2}{3} q'} = \frac{\kappa}{3} F' = q \frac{\epsilon_a - 1}{3}$$

Hence

$$\epsilon_0 - 1 = \frac{\epsilon_a - 1}{1 - \frac{\epsilon_a - 1}{3} + \frac{q'}{3} (\epsilon_a - 1)^2} = \left[1 + \frac{\epsilon_a - 1}{3} + \left(\frac{1}{q} - \frac{q'}{3} \right) (\epsilon_a - 1)^2 \right] (\epsilon_a - 1) \quad (17)$$

Thus $\frac{q'}{3}$ occurs here together with the larger term $\frac{1}{q}$.

If the demagnetizing field is negligible as in the case of a thin long tube $\epsilon - 1 = \kappa F' = q(\epsilon_a - 1)$ where ϵ is the effective susceptibility. Hence by (14'')

$$\epsilon_0 - 1 = \frac{\epsilon_a - 1}{1 - \frac{p}{3} (\epsilon_a - 1) + \frac{q'}{3} (\epsilon_a - 1)^2} \dots \dots \dots (17')$$

If the sample has the form of a thin slab normal to the lines of force

$$\epsilon_0 - 1 = \frac{\epsilon_a - 1}{1 - \frac{1+2q}{3}(\epsilon_a - 1) + \frac{q'}{3}(\epsilon_a - 1)^2} \dots (17'')$$

Space lattice of spherical holes.

From (14'') we get for this case to within the second power of $(\epsilon_0 - 1)^2$

$$\epsilon - 1 = \frac{q(\epsilon_0 - 1)}{1 + \frac{p}{3}(\epsilon_0 - 1) - p\left(\frac{2}{9} - \frac{p'}{3q}\right)(\epsilon_0 - 1)^2}$$

where p' is the same function of h as q' . The corresponding formula for the space lattice of spheres is

$$\epsilon - 1 = \frac{q(\epsilon_0 - 1)}{1 + \frac{p}{3}(\epsilon_0 - 1) - \frac{q'}{3}(\epsilon_0 - 1)^2}$$

The term $\frac{p'}{3q}$ thus tends to reconcile the two expressions. However for the case of touching spheres or touching holes the space lattice of holes has a higher ϵ than the space lattice of spheres even though q is made the same for both. This means that the continuous path of the flux between the holes contributes to a high value of the effective ϵ . It thus becomes apparent that q and ϵ_0 alone do not suffice to determine ϵ even if the structure is on the average isotropic. The correction in $(\epsilon_0 - 1)^2$ may therefore be never applied with certainty and an estimate of its amount is all that the present theory can offer.

SUMMARY.

1. The consideration of the effects of the demagnetizing field for various models of the powder shows that to within the first order terms the correction is the same for all models considered and may be expressed by the fact that the force on a sphere of the powder is equal to the force which would be exerted on the material if it were moulded into a solid sphere instead of being powdered.

2. Different models give results differing in the second order terms in the demagnetizing field.

APPENDIX.

1. It is shown in MAXWELL'S Treatise that

$$Y_c^{(m)} = \frac{(-)^n}{n!} r^{m+1} D_c^m \frac{1}{r}.$$

Now

$$Y_c^m = \frac{2n!}{2^{n+m} (n!)^2} \Theta_n^m \cdot 2 \cos m \Phi$$

and

$$P_n^m = \frac{2n!}{2^n (n-m)! n!} \Theta_n^m.$$

Hence

$$\frac{2 P_n^m (\cos \vartheta) \cos m \Phi}{r^{m+1}} = \frac{(-)^n 2^m}{(n-m)!} D_c^m \frac{1}{r}$$

It is also well known that

$$\frac{P_n}{r^{n+1}} = \frac{(-)^n}{n!} \frac{\partial^n \left(\frac{1}{r} \right)}{\partial z^n}.$$

These two equations may be combined in:

$$\frac{\cos m \Phi P_n^m (\cos \vartheta)}{r^{n+1}} = \frac{(-)^n 2^m b_m}{(n-m)!} D_c^m \left(\frac{1}{r} \right) \dots \dots (1A)$$

where

$$b_0 = 1; \quad b_1 = b_2 = \dots = \frac{1}{2}.$$

2. To show that:

$$D_c^m \left(\frac{r^\nu P_\nu^{\mu} (\cos \vartheta) \cos \mu \Phi}{b_\mu} \right) = \frac{(-)^m (r + \mu)! r^{\nu-n} P_{\nu-n}^{\nu+m} (\cos \vartheta) \cos (m + \mu) \Phi}{2^m (r + \mu - n \cdot m)! b_{m+\mu}} \quad (2A)$$

We consider the following cases:

$$(I). \quad \mu = m = 0$$

We must show that

$$\frac{\partial^n}{\partial z^n} (r^\nu P_\nu (\cos \vartheta)) = \frac{\nu! r^{\nu-n}}{(\nu-n)!} P_{\nu-n} (\cos \vartheta).$$

Proof. Using LAPLACE'S integral

$$P_\nu (\cos \vartheta) = \frac{1}{\pi} \int_0^\pi (\cos \vartheta + i \sin \vartheta \cdot \cos \Phi)^\nu d\Phi$$

we have $r^\nu P_\nu (\cos \vartheta) = \frac{1}{\pi} \int_0^\pi (z + i \rho \cos \Phi)^\nu d\Phi$ where $\rho = \sqrt{x^2 + y^2}$.

whence the formula follows on differentiation.

$$(II). \quad n = m, \quad \mu = 0$$

We must show that:

$$D_c^m (r^n P_n (\cos \vartheta)) = \frac{(-)^m}{2^m} r^{n-m} P_{n-m}^m (\cos \vartheta) \cdot 2 \cos m\vartheta$$

Proof. Since $\varrho^2 = \xi\eta$ we have

$$r^n P_n = \sum_p \frac{(-)^p n! z^{n-2p} \xi^p \eta^p}{2^{2p} (p!)^2 (n-2p)!}$$

Operating on this with D_c^m and observing that

$$P_{n-m}^m (\cos \vartheta) = \frac{n!}{2^m} \sin^m \vartheta \sum_p \frac{(-)^p \cos^{n-2m-2p} \vartheta \sin^{2p} \vartheta}{(n-2m-2p)! 2^{2p} p! (m+p)!}$$

the above written formula follows. An analogous formula holds of course for the operator D_s^m .

$$(III). \quad m \neq 0, \quad \mu \geq 1$$

Using (1_A) and (II), (2_A) is found.

$$(IV). \quad m = 0$$

This is also verified without difficulty.

Physics. — “On the Heat of Mixing of Normal and Associating Liquids.” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of September 30, 1922).

1. In connection with a study by J. R. KATZ (published in „Verlag der Wis- en Naturk. Afdeeling Kon. Akad. v. Wetensch.” Vol. XXXI, nos 5/6, p. 333—336) I wish to make a few remarks on the heat of mixing of liquids, also in reference to the quantity a/v^2 (or a/l^2).

Different authors, among others VAN DER WAALS and myself, made use of approximations some time ago, which seemed permissible; but which gave no account, not even in approximation, of the heat-effect, which is sometimes very slight, especially for normal substances. For here the case presented itself that the neglected quantities $((v-b)^2$ by the side of v^2 , p by that of a/v^2) would give a term of higher order of magnitude in the results than that which results from the not neglected part. The latter term appears to be of the order of magnitude $(b_2\sqrt{a_1}-b_1\sqrt{a_2})^2$, whereas that of the neglected part — yielding a term with $(p + a/v^2) \Delta v$ — is of the order $b_2\sqrt{a_1}-b_1\sqrt{a_2}$ on account of Δv ; hence, when the difference of the critical pressures of the components is small, the neglected part will have a much greater value than the not neglected part.

And besides: While the first part — referring to the change of the potential energy without reference to the contraction — will always be *positive*, the second (neglected) part — which is in connection with the *volume contraction* Δv — is nearly always *negative*. In “quasi-ideal” mixtures of two liquids (i.e. liquids the critical pressures of which are about equal), the effect will nearly always be *negative* (i.e. heat is *liberated*), and not *positive*, as the earlier theoretical derivation indicated. In liquids the critical pressures of which are not about equal, sometimes differ even considerably, it will entirely depend on circumstances (relation of the a 's and b 's inter se, value of the mixing ratio x) whether the result will be positive or negative.

In associated components, where Δv can become much greater than in mixtures of normal components (generally the critical pressures also differ much more from each other), the above ratios will

be more greatly accentuated, and the negative term with $(p + a_{1,2})\Delta v$ will predominate still more.

Already BAKHUIS ROOZEBOOM — now about twenty years ago — drew my attention to the insufficiency of the approximative expression, but at the time we attributed this to other causes¹⁾, thinking that — especially in quasi-ideal mixtures — the possible volume-contraction would probably be quite negligible. Not until 1912, when in a letter my friend Prof. KREMANN at Graz put a question to me on this subject, was I led to carry out the perfectly accurate calculation of the quantity Δv ²⁾.

In what follows I may be allowed to give the exact theory, first of all of mixtures of normal components. Here too the perfectly accurate derivation appears to be by no means more difficult or longer than the approximated derivation, and the result is almost equally simple. The same thing is found here as before with the exact derivation of the equations of the spinodal and the plaitpoint line³⁾. There the perfectly accurate results are even simpler than the earlier approximated expressions.

2. Heat of mixing of normal components.

From the well-known expression for the total energy

$$e = e' + kT - \frac{a}{v} + pv,$$

in which the energy constant e' is $= n_1 e'_1 + n_2 e'_2$, and the heat capacity at constant (infinitely great) volume $k = n_1 k_1 + n_2 k_2$, we find for the pure components:

$$\left. \begin{aligned} e_1^{\circ} &= e'_1 + k_1 T - \frac{a_1}{v_1^{\circ}} + pv_1^{\circ} \\ e_2^{\circ} &= e'_2 + k_2 T - \frac{a_2}{v_2^{\circ}} + pv_2^{\circ} \end{aligned} \right\}.$$

For the *integral* heat of mixing of n_1 gr. mol. of one component and n_2 gr. mol. of the other component the expression

¹⁾ Inaccuracy of VAN DER WAALS' equation of state; non-validity of BERTHELOT's assumption $a_{12} = \sqrt{a_1 a_2}$, etc. But since then I have got more than ever convinced of the absolute validity (in liquids) of the said equation and B's assumption. Of course a and b then have *other* values than in the gaseous state, but this need, of course, not be considered here.

²⁾ Later inserted summarized in his valuable — unfortunately too little known — book: "Die Eigenschaften der binären Flüssigkeitsgemische etc." (Sammlung (HERZ) chemischer Vorträge Bd. 23, Stuttgart, Enke, 1916); see p. 170—171.

³⁾ These Proc. Vol. VII, p. 646; Vol. VIII, p. 33.

$$w = - \left(\frac{a}{v} - n_1 \frac{a_1}{v_1^0} - n_2 \frac{a_2}{v_2^0} \right) + p (v - n_1 v_1^0 - n_2 v_2^0) \quad (a)$$

is at once found from

$$w = e - (n_1 e_1^0 + n_2 e_2^0)$$

Now

$$\frac{a}{v} = \frac{a}{v_0} + \left(\frac{a}{v} - \frac{a}{v_0} \right) = \frac{a}{v_0} - \frac{a}{v v_0} \Delta v,$$

in which $v_0 = n_1 v_1^0 + n_2 v_2^0$, and $v - v_0 = \Delta$ is written. Further $a = (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2$, and from this follows:

$$\frac{a}{v_0} = \left(n_1 \frac{a_1}{v_1^0} + n_2 \frac{a_2}{v_2^0} \right) - n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0}.$$

Hence:

$$w = n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0} + \left(p + \frac{a}{v v_0} \right) \Delta v \quad (1)$$

Remarks. a. Formerly ¹⁾ the following equation was written:

$$\frac{a}{v} = \frac{a}{v} + \left(\frac{a}{v^2} (v-b) + p (v-b) - (n_1 + n_2) RT \right),$$

on account of the equation of state. This gives:

$$\frac{a}{v} = \frac{a}{v^2} (2v-b) + p (v-b) - (n_1 + n_2) RT = \frac{a}{b} \left(1 - \left(\frac{v-b}{v} \right)^2 \right) + p (v-b) - (n_1 + n_2) RT,$$

hence:

$$e = e' + \left(k + (n_1 + n_2) R \right) T - \frac{a}{b} \left(1 - \frac{(v-b)^2}{v^2} \right) + pb,$$

for which $e = e' + k' T - a/b$ was written — with an apparently perfectly justifiable neglect of some terms. Then we get:

$$w = n_1 n_2 \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b b_1 b_2}.$$

It is seen that the very essential term $\frac{a}{v v_0} \Delta v$ is omitted.

b. We might also have written:

$$\frac{a}{v} = n_1 \frac{a_1}{v_1} + n_2 \frac{a_2}{v_2} - n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2},$$

in which $v_1 = \frac{\partial v}{\partial n_1}$ and $v_2 = \frac{\partial v}{\partial n_2}$. For according to a property of the

¹⁾ Cf. among others Zeitschr. f. physik. Ch. 63, p. 219 (1908).

homogeneous functions of the first degree with regard to n_1 and n_2 , we have $v = n_1 v_1 + n_2 v_2$. And further according to (a):

$$w = n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2} + n_1 \left(\frac{a_1}{v_1^0} - \frac{a_1}{v_1} \right) + n_2 \left(\frac{a_2}{v_2^0} - \frac{a_2}{v_2} \right) + p (n_1 (v_1 - v_1^0) + n_2 (v_2 - v_2^0)),$$

or also

$$w = n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2} \cdot \left(p + \frac{a_1}{v_1 v_1^0} \right) n_1 \Delta v_1 + \left(p + \frac{a_2}{v_2 v_2^0} \right) n_2 \Delta v_2, \quad (1^a)$$

which expression will at once appear to be useful.

Here is $v_1 - v_1^0 = \Delta v_1$ and $v_2 - v_2^0 = \Delta v_2$ and evidently we have $\Delta v = v - v_0 = (n_1 v_1 + n_2 v_2) - (n_1 v_1^0 + n_2 v_2^0) = n_1 \Delta v_1 + n_2 \Delta v_2$.

For the differential heats of mixing $w_1 = \frac{\partial w}{\partial n_1}$ and $w_2 = \frac{\partial w}{\partial n_2}$ we now have from (1^a):

$$w_1 = n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v_1 v_2} \frac{\partial}{\partial n_1} \left(\frac{n_1}{v} \right) + \left(p + \frac{a_1}{v_1 v_1^0} \right) \Delta v_1,$$

or as $\frac{\partial}{\partial n_1} \left(\frac{n_1}{v} \right) = \frac{v - n_1 v_1}{v^2} = \frac{n_2 v_2}{v^2}$:

$$w_1 = n_2^2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v^2 v_1} + \left(p + \frac{a_1}{v_1 v_1^0} \right) \Delta v_1$$

Likewise

$$w_2 = n_1^2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v^2 v_2} + \left(p + \frac{a_2}{v_2 v_2^0} \right) \Delta v_2$$

. . . (2)

¹⁾ In these differentiations many parts have not been taken into account. For in general v_1 and v_2 are still functions of n_1 and n_2 . But as the neglected parts in w_1 and w_2 can always be represented by $z_1 = \frac{\partial z}{\partial n_1}$ and $z_2 = \frac{\partial z}{\partial n_2}$, in which z , just as w , will always be a homogeneous function of the first degree with respect to n_1 and n_2 , necessarily $n_1 z_1 + n_2 z_2$ will have to be = 0, $n_1 w_1 + n_2 w_2$ already being = w according to (2). Now also $n_1 z_1 + n_2 z_2 = z$, hence z is identically = 0, hence also z_1 and z_2 .

It would indeed not be difficult to show directly the disappearance of the parts z_1 and z_2 , which have been left out of account. As to z_1 , we get the result:

$$\frac{1}{v} \left(n_1 \frac{a_1}{v_1} + n_2 \frac{a_2}{v_2} \right) \left(n_1 \frac{\partial v_1}{\partial n_1} + n_2 \frac{\partial v_2}{\partial n_1} \right),$$

in which the last factor will disappear in consequence of $\frac{\partial v_2}{\partial n_1} = \frac{\partial v_1}{\partial n_2}$, as v_1 is a homogeneous function of the 0th degree with respect to the molecular numbers n_1 and n_2 .

For liquids p may of course always be cancelled against the so much greater molecular pressure a/v^2 .

We will just mention that the earlier — inaccurate — expressions were:

$$w_1 = n_2 \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b^2 b_1} ; \quad w_2 = n_1 \frac{(b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b^2 b_2}.$$

3. Volume contraction with normal components.

We must now try to find an expression for Δv , and then also for Δv_1 and Δv_2 , in order to be able to substitute in (1) and (2), and to form an opinion of the order of magnitude of the different parts. As

$$\Delta v = v - v_0 = v - (n_1 v_1^0 + n_2 v_2^0),$$

we have also:

$$\Delta v = b - (n_1 b_1 + n_2 b_2) + (v - b) - n_1 (v_1^0 - b_1) - n_2 (v_2^0 - b_2).$$

Now $b = n_1 b_1 + n_2 b_2$, hence after application of the equation of state, there remains:

$$\Delta v = \frac{(n_1 + n_2) RT}{p + a/v^2} - \frac{n_1 RT}{p + a_1/v_1^2} - \frac{n_2 RT}{p + a_2/v_2^2},$$

i.e. with neglect of p :

$$\Delta v = RT \left[(n_1 + n_2) \frac{v^2}{a} - n_1 \frac{v_1^0{}^2}{a_1} - n_2 \frac{v_2^0{}^2}{a_2} \right],$$

or

$$\Delta v = \frac{RT}{a a_1 a_2} \left[(n_1 + n_2) (n_1 v_1^0 + n_2 v_2^0)^2 a_1 a_2 - n_1 v_1^0{}^2 a a_2 - n_2 v_2^0{}^2 a a_1 \right] + \frac{RT}{a} (n_1 + n_2) \left(2 \Delta v (n_1 v_1^0 + n_2 v_2^0) + (\Delta v)^2 \right),$$

as $v = (n_1 v_1^0 + n_2 v_2^0) + \Delta v$. In consequence of this, with $a = (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2$:

$$\begin{aligned} \Delta v - \frac{(n_1 + n_2) RT}{a} \left(2 \Delta v (n_1 v_1^0 + n_2 v_2^0) + (\Delta v)^2 \right) &= \\ = \frac{RT}{a a_1 a_2} \left[(n_1 + n_2) (n_1 v_1^0 + n_2 v_2^0)^2 a_1 a_2 - (n_1 v_1^0{}^2 a_2 + n_2 v_2^0{}^2 a_1) (n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2 \right], \end{aligned}$$

which, worked out with neglect of Δv by the side of $2v$, and putting $n_1 + n_2 = 1$ at RT , gives:

$$\Delta v \left(1 - \frac{2 RT}{a/v} \right) =$$

$$\begin{aligned}
&= \frac{RT}{a a_1 a_2} n_1 n_2 \left[\left\{ n_1 v_1^{\circ 2} + 2(n_1 + n_2) v_1^{\circ} v_2^{\circ} + n_2 v_2^{\circ 2} \right\} a_1 a_2 - \right. \\
&\quad \left. - \left\{ n_1 v_2^{\circ 2} a_1^2 + 2(n_1 v_1^{\circ 2} a_2 + n_2 v_2^{\circ 2} a_1) \sqrt{a_1 a_2} + n_2 v_1^{\circ 2} a_2^2 \right\} \right] \\
&= \frac{RT}{a a_1 a_2} n_1 n_2 \left[n_1 \left\{ v_1^{\circ} a_2 \sqrt{a_1} \left((v_1^{\circ} + 2v_2^{\circ}) \sqrt{a_1} - 2v_1^{\circ} \sqrt{a_2} \right) - v_2^{\circ 2} a_1^2 \right\} + \right. \\
&\quad \left. + n_2 \left\{ v_2^{\circ} a_1 \sqrt{a_2} \left((v_2^{\circ} + 2v_1^{\circ}) \sqrt{a_2} - 2v_2^{\circ} \sqrt{a_1} \right) - v_1^{\circ 2} a_2^2 \right\} \right] \\
&= \frac{RT}{a a_1 a_2} n_1 n_2 \left[n_1 \left\{ 2v_1^{\circ} a_2 \sqrt{a_1} (v_2^{\circ} \sqrt{a_1} - v_1^{\circ} \sqrt{a_2}) + a_1 (v_1^{\circ 2} a_2 - v_2^{\circ 2} a_1) \right\} + \right. \\
&\quad \left. + n_2 \left\{ 2v_2^{\circ} a_1 \sqrt{a_2} (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) + a_2 (v_2^{\circ 2} a_1 - v_1^{\circ 2} a_2) \right\} \right] \\
&= \frac{RT}{a a_1 a_2} n_1 n_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) \left[n_1 \left\{ (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) a_1 - 2v_1^{\circ} a_2 \sqrt{a_1} \right\} + \right. \\
&\quad \left. + n_2 \left\{ - (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) a_2 + 2v_2^{\circ} a_1 \sqrt{a_2} \right\} \right].
\end{aligned}$$

For the form between [] we may further write:

$$\begin{aligned}
&n_1 a_1 (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) - n_2 a_2 (v_1^{\circ} \sqrt{a_2} + v_2^{\circ} \sqrt{a_1}) - 2n_1 v_1^{\circ} a_2 \sqrt{a_1} + 2n_2 v_2^{\circ} a_1 \sqrt{a_2} \\
&= -n_1 a_1 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) - n_2 a_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) + \\
&\quad + 2a_1 \sqrt{a_2} (n_1 v_1^{\circ} + n_2 v_2^{\circ}) - 2a_2 \sqrt{a_1} (n_1 v_1^{\circ} + n_2 v_2^{\circ}),
\end{aligned}$$

so that we finally get:

$$\Delta v \left(1 - \frac{2RT}{a/v} \right) = \frac{RT}{a a_1 a_2} n_1 n_2 (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1}) \left[\frac{2v_1^{\circ} (\sqrt{a_1} - \sqrt{a_2}) \sqrt{a_1 a_2} - (n_1 a_1 + n_2 a_2) (v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1})}{\dots} \right] \quad (3)$$

This almost quite exact result (only p has been neglected, and in the 1st member Δv by the side of $2v$) shows that Δv will be of the order $\delta = v_1^{\circ} \sqrt{a_1} - v_2^{\circ} \sqrt{a_1}$, so that w consists of two parts, of which the first is of the order δ^2 (cf. equation (1)), the second of the order δ . When the critical pressures differ little, δ is very small, and of the small heat of mixing w the second part (neglected before) will certainly predominate.

In the case that the *critical pressures differ little*, expression (3) can be considerably simplified. For then $v_1^{\circ} \sqrt{a_2} - v_2^{\circ} \sqrt{a_1} = 0$ can be put between [], and there remains:

$$\Delta v \left(1 - \frac{2RT}{a/v}\right) = \frac{2RT}{a/v_0} n_1 n_2 \left(1 - \frac{v_2^0 \sqrt{a_1}}{v_1^0 \sqrt{a_2}}\right) \frac{v_1^0 \sqrt{a_2} (\sqrt{a_1} - \sqrt{a_2})}{\sqrt{a_1 a_2}}$$

But because then $\sqrt{a_2} = \frac{v_2^0}{v_1^0} \sqrt{a_1}$, $\sqrt{a_1} - \sqrt{a_2} = \frac{v_1^0 - v_2^0}{v_1^0} \sqrt{a_1}$,

$$\text{hence } \Delta v \left(1 - \frac{2RT}{a/v}\right) = \frac{2RT}{a/v_0} n_1 n_2 \left(1 - \sqrt{\frac{p_{k_1}}{p_{k_2}}}\right) (v_1^0 - v_2^0) \quad (3a)$$

As for ordinary substances in liquid state (below the boiling-point) $a/v = 7RT_k$, and in the second member $v_0 = v$ may be put, we find with $T/T_k = m$:

$$\Delta v = \frac{2/7 m}{1 - 2/7 m} n_1 n_2 \left(1 - \sqrt{\frac{p_{k_1}}{p_k}}\right) (v_1^0 - v_2^0) \quad (3b)$$

If e.g. $m = 1/2$, we have with $n_1 = 1-x$, $n_2 = x$ for Δv the value $1/2 x(1-x)(1-\sqrt{p_{k_1}/p_k})(v_1^0 - v_2^0)$, so that the *maximum* contraction (at $x = 1/2$) becomes $= 1/24 (1-\sqrt{p_{k_1}/p_k})(v_1^0 - v_2^0)$ — hence very small and of the order $1-\sqrt{p_{k_1}/p_k}$.

With regard to the *sign* of Δv it may be pointed out that $b_1 > b_2$, e.g. $b_1 = \theta b_2$, corresponds with $v_1^0 > v_2^0$. Then a_1 is approximately $= \theta^2 a_2$, so that a_1/b_1 becomes $= \theta a_2/b_2$ or $T_{k_1} > T_{k_2}$. But from this it ensues that p_{k_1} is generally somewhat greater than p_{k_2} , in consequence of which $1-\sqrt{p_{k_1}/p_k}$ becomes negative. And the reverse when v_1^0 should be $< v_2^0$. The quantity Δv will, therefore, nearly always be *negative*, in other words volume contraction will take place.

With regard to the differential variations of volume $\Delta v_1 = v_1 - v_1^0 = \frac{\partial(\Delta v)}{\partial n_1}$ and $\Delta v_2 = v_2 - v_2^0 = \frac{\partial(\Delta v)}{\partial n_2}$, from the approximated expression (3a) follows, when a/v is considered constant in the correction term of the 1st member:

$$\Delta v_1 \left(1 - \frac{2RT}{a/v}\right) = 2RT n_2 (1-\sqrt{p_{k_1}/p_k}) (v_1^0 - v_2^0) \frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a}\right)$$

In approximation $v_1^0 \sqrt{a_2} = v_2^0 \sqrt{a_1}$ was taken, so that $\sqrt{a_1}$ is $= \frac{v_1^0}{v_2^0} \sqrt{a_2}$ and $\sqrt{a} = n_1 \sqrt{a_1} + n_2 \sqrt{a_2} = \sqrt{a_2} \left(n_1 \frac{v_1^0}{v_2^0} + n_2\right) = \frac{v_0}{v_2^0} \sqrt{a_2}$.

In consequence of this $\frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a}\right)$ becomes $= \frac{\partial}{\partial n} \left(\frac{n_1 v_0^3 v_2^0}{a_2 v_0^2}\right) = \frac{v_2^0}{a_2} \frac{\partial}{\partial n_1} \left(\frac{n_1}{v_0}\right)$, in which $\frac{\partial}{\partial n_1} \left(\frac{n_1}{v_0}\right) = \frac{v_0 - n_1 v_1^0}{v_0^2} = \frac{n_2 v_2^0}{v_0^2}$. Hence we have

$\frac{\partial}{\partial n_1} \left(\frac{n_1 v_0}{a} \right) = n_2 \frac{v_2^0}{v_0^0} \frac{v_2^0}{a_2} = n_2 \frac{v_2^0}{a}$; therefore with the same approximation as (3a):

$$\text{and } \left. \begin{aligned} \Delta v_1 \left(1 - \frac{2RT}{a/v} \right) &= \frac{2RT}{a/v_2^0} n_2^2 (1-V) (v_1^0 - v_2^0) \\ \Delta v_2 \left(1 - \frac{2RT}{a/v} \right) &= \frac{2RT}{a/v_1^0} n_1^2 (1-V) (v_1^0 - v_2^0) \end{aligned} \right\} \dots (4a)$$

We now duly get again $n_1 \Delta v_1 + n_2 \Delta v_2 = \Delta v_1$, because $n_1 n_2^2 \frac{v_2^0}{a} + n_2 n_1^2 \frac{v_1^0}{a} = n_1 n_2 \frac{v_0}{a}$.

4. Substitution of (3^b) in (1).

We get for w , after substitution of (3^a) in (1), with omission of the external pressure p :

$$w = n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0} + \frac{a^{1/2} m}{v v_0 1 - \frac{2}{7} m} n_1 n_2 \frac{v_1^0 \sqrt{a_2} - v_2^0 \sqrt{a_1}}{v_1^0 \sqrt{a_2}} (v_1^0 - v_2^0),$$

or

$$w = n_1 n_2 \left[\frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0} - \frac{1 - \frac{2}{7} m}{1 - \frac{2}{7} m} \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2}) (v_1^0 - v_2^0) \sqrt{a}}{v v_1^0 v_2^0} \right],$$

when $v_2^0/v_0 \sqrt{a}$ is substituted for $\sqrt{a_2}$. With $m = 1/2$ and $v = v_0$, this passes into

$$w = \frac{n_1 n_2}{v_0 v_1^0 v_2^0} (v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2}) \left[(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2}) - \frac{1}{6} (v_1^0 - v_2^0) \sqrt{a} \right] \dots (5b)$$

The factor $1/6$ is, of course, somewhat different, when $m = T/T_c$ is not $= 1/2$. When the critical pressures are equal, the foregoing factor is $= 0$, hence also the total heat of mixing. But when these pressures do not differ too much, the first term between [] will all the same be small with regard to the second, and in approximation

$$w = - \frac{1}{6} \frac{n_1 n_2}{v_0 v_1^0 v_2^0} (v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2}) (v_1^0 - v_2^0) \sqrt{a} \dots (5c)$$

may be written.

But however this be, we shall always be allowed to write:

$$w = n_1 n_2 \frac{\beta}{v_0 v_1^0 v_2^0} ; \quad w_1 = n_2^2 \frac{\beta}{v_0^2 v_1^0} ; \quad w_2 = n_1^2 \frac{\beta}{v_0^2 v_2^0},$$

or, as $v_0 = n_1 v_1^0 + n_2 v_2^0 = (1-x) v_1^0 + x v_2^0 = v_1^0 + x(v_2^0 - v_1^0) =$

$= v_1^0 (1 + rx)$, when $\frac{v_2^0 - v_1^0}{v_1^0} = r$ (hence $\frac{v_2^0}{v_1^0} = 1 + r$) is put, and with $\frac{\beta}{(v_1^0)^2} = \alpha$:

$$w = x(1-x) \frac{\alpha}{(1+rx)(1+r)}; \quad w_1 = \frac{x^2 \alpha}{(1+rx)^2}; \quad w_2 = \frac{(1-x)^2 \alpha}{(1+rx)^2(1+r)}, \quad (6)$$

the old expressions, but in which α has now a somewhat different value than before, and will also be dependent on the temperature (through m).

When in approximation

$$w = \frac{\alpha}{v v_0} \Delta v = \frac{\alpha}{v^2} \Delta v$$

is written for (1) with omission of the first part, which is generally much smaller, we get approximately:

$$\frac{w}{\Delta v} = \frac{\alpha}{v^2} \dots \dots \dots (7)$$

If the critical pressures of different substances do not diverge too much, also the values of α/v_2 do not lie far apart in mixtures of different pairs of substances, and we shall find values of at least the same order of magnitude for the quotient $\frac{w}{\Delta v}$; a result to which also Mr. KATZ came experimentally in his latest paper (*loc.cit.*)¹⁾ — at least as far as volume-contraction and heat of imbibition of amorphous and crystalline swelling substances is concerned. That the ratios there are quite analogous to those of liquid mixtures is owing to this, that when one of the components is *solid*, it must first be reduced to the liquid state, whence the pure heat of melting of this components is simply added to w . But if Δv predominates, also *this* heat might be omitted with respect to the second part.

At any rate we shall never find exactly α/v_2 for $w/\Delta v$, because the omitted part can never be entirely disregarded. For this reason also the values of $w/\Delta v$ will differ somewhat, even with almost equal values of α/v_2 , which was also found by KATZ.

¹⁾ The curves of Fig. 1 and 2 are no hyperbolae, but *oblique parabolae*, as according to (6) w is $= \frac{x(1-x)}{1+rx} \frac{\alpha}{1+r}$. If r were $= 0$ ($v_2^0 = v_1^0$), the curve of the integral heat of mixing (i.e. $1-x$ gr. mol. of I + x gr. mol. of II) would be a pure parabola. If, however, v_2^0 is not $= v_1^0$, the top of the parabola will have been displaced somewhat to the side of the component with the smallest molecular volume, as is easy to verify. From $\frac{\partial w}{\partial x} = 0$ we find $x = 1/(1 + \frac{1}{1+r})$, which gives $x = 1/2$ for $r = 0$, but $x < 1/2$ for $r > 0$. ($v_2^0 > v_1^0$).

The values of a/v^2 in our above formulae always refer exclusively to the *liquid mixture*, even for *solid* components, for as we already remarked above: this solid component must first be thought liquid, so that after all we have always to do with *liquid* mixtures.

Now that through the formulae derived by us above, the *absolute* values of w and Δv are known, which Mr. KATZ so eagerly desired, the problem has become clearer. Also when the components should be associated, everything remains essentially the same, as I will shortly show in a concluding paper. But then the preponderating influence of Δv will still be more pronounced, in consequence of the great variation of volume on dissociation of the double molecules.

And finally as regards the "important as yet undiscovered principles of the laws that govern molecular attraction" — I believe that this principle too was solved long ago¹⁾. This subject will also be discussed more fully in our concluding paper.

Tavel sur Clarens (Suisse), September 1922.

¹⁾ Compare my papers in These Proc. Vol. XVIII N^o. 8, p. 1220—1235, and following numbers; in the Journ. de Ch. physique **14**, p. 1 et seq. (1916); in the Z. f. anorg. und allg. Chemie **104**, p. 57—156 (1918); in the Ch. Weekbl. of 1918 (p. 1124); in These Proc. Vol. XXI N^o. 5, p. 644—655, and the J. de Ch. ph. **16**, 411 (1919), which possibly have escaped Mr. KATZ's notice.

Histology. — *“On the Regeneration of Sensitive End-corpuscles after section of the nerve”*. By Prof. J. BOEKE.

(Communicated at the meeting of September 30, 1922).

During the process of regeneration of the motor endplates of striated muscles we are in a position to observe not only that the nerve-fibers put forth new shoots again and unite with the muscle-fibers to form new end-plates, but also that all the surrounding tissue elements: the connective tissue as well as the muscle-fibers, the nerve-sheaths and the axis-cylinders of the nerves themselves, play a part in the regeneration process and are instrumental in ensuring its success.

In the case of sensitive nerve-endings it is more difficult to observe this procedure: 1° because there is a greater variety in the shape of these endings than in that of the motor end-plates, 2° because many more varieties occur side by side in the same environment, and 3° because sensory endings generally offer greater difficulty in establishing the relation between the nerve-fibers and the surrounding cells than motor end-plates do.

Now in the cere of the duck's bill there are two sorts of sensory end-bodies, viz. those of GRANDRY and HERBST, which are very well adapted to such an investigation by their simple, well-defined structure.

We examined the regeneration after cutting the nerve. The operation was well sustained by the animals and in a short time the wound was healed in primam (among 24 cases one inconsiderable suppuration) without any injury to the animals.

After 4—5 days the severed nerves were completely degenerated; nothing was left of the axis-cylinder except a few granules staining brownish black by BIELSCHOWKY's method. After some days these also disappeared.

An alteration of GRANDRY's tactile cells or of HERBST's core-cells, described by GASIOROWSKI years ago after cutting the nerve, consisting in shrivelling of the cells and bulging and wrinkling of the nuclei, I have not been able to detect. In agreement with the aspect of the soles of the motor endings the protoplasm became more coarse-grained, swollen, while the impression was given that in the core

of HERBST's corpuscles there were more nuclei than the normal corpuscle presents. There also seemed to exist a slight increase in the number of the capsule-cells of GRANDRY's corpuscles.

While regenerating the nerve-fibers follow the old nerve-courses (which have changed into strands of BÜNGNER), and pass again into the primary corpuscles. It seems, however, that all along also new corpuscles, especially GRANDRY's corpuscles, are formed, in which process sheath-cells (lemnoblasts) grow larger and become tactile cells, as HERINGA has established as to embryological development. As soon as the nerve-fibers have reached the tactile cells of GRANDRY, they branch out, grow sinuously round them, always embedded in the protoplasm of the capsule-cells and at length force their way between the tactile cells. Directly after this the neurofibrils begin to branch, broadening reticulations appear, which gradually spread between the tactile cells, first as a delicate retiform structure, afterwards as a close-mesh network. In this way the whole interspace between the two tactile cells is occupied again by a net-shaped neurofibrillar nerve-plate.

Two things strike us here as being remarkable:

First of all that in the beginning of the process of regeneration the nerve-fibers bend round the tactile cells in various convolutions and ramifications, but that in the following stages (after 2 or 3 months) this process is less pronounced, so that gradually the normal condition asserts itself in the same way as with the motor end-plates; secondly that neither the nerve-fibers themselves nor their terminal branches and terminal broadening ever run freely, but always remain enclosed in the protoplasm of the conducting cells and the capsule-cells, and that directly when they are within reach of the tactile cells, a peculiar network is formed around them, inside the protoplasm of the tactile cells, which could also be demonstrated, in complete distribution, in the normal corpuscles of GRANDRY; lastly that here the process of regeneration of the intraprotoplasmic network shows itself first round the end-branches (end-reticulations and end-knots) of the nerve-fibers and then appears to extend gradually over the whole extent of the flat tactile-cells. The whole regeneration-process takes two or three months.

In the case of HERBST's corpuscles the in-growing nerve-fibers also follow the old nerve-tracks. At their point of entrance into the core of the corpuscle we see also here that the nerve-fiber not only proceeds linearly into the protoplasm of the syncytially connected cells of the core, but also that it throws out its branches and passes with many convolutions through the protoplasm, so that the aspect

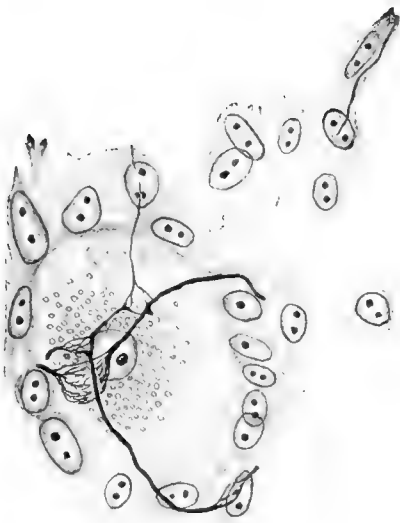


Fig. 1. GRANDRY's corpuscle. 36 days after cutting the nerve. Initial stage of the surface-enlargement in the neurofibrillar apparatus of the nerve-fibrils that grow round the tactile cells. Transverse section.

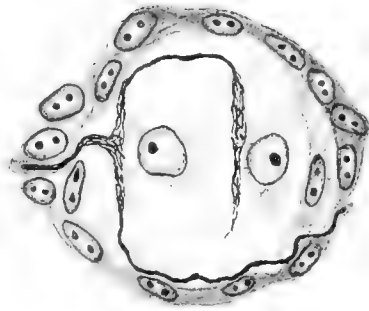


Fig. 2. GRANDRY's corpuscle, 46 days after cutting the nerve. Complete regeneration, double growth round the tactile cells. Longitudinal section.

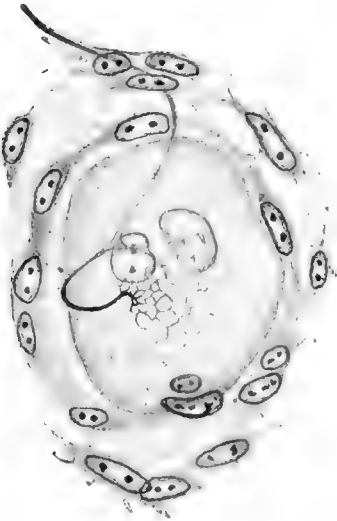


Fig. 3.

GRANDRY's corpuscle. 42 days after the cutting of the nerve. Transverse section of the same end-body at different planes. Splitting of the in-growing nerve-thread. Intrusion between the tactile cells, formation of a protoplasmic network (receptive substance, periterminal network) round the end-buds of the neurofibrillar nerve-apparatus.



Fig. 4.

of the whole structure becomes much more complicated than that of the primary nerve-fiber of the normal HERBST-corpuseles. However, here also the normal relations gradually assert themselves. I have not been able to ascertain whether new HERBST-corpuseles are forming in the course of the regeneration process.

Round the inner core in HERBST's corpuseles are disposed a large number of connective-tissue lamellae, separated by lymphspaces.

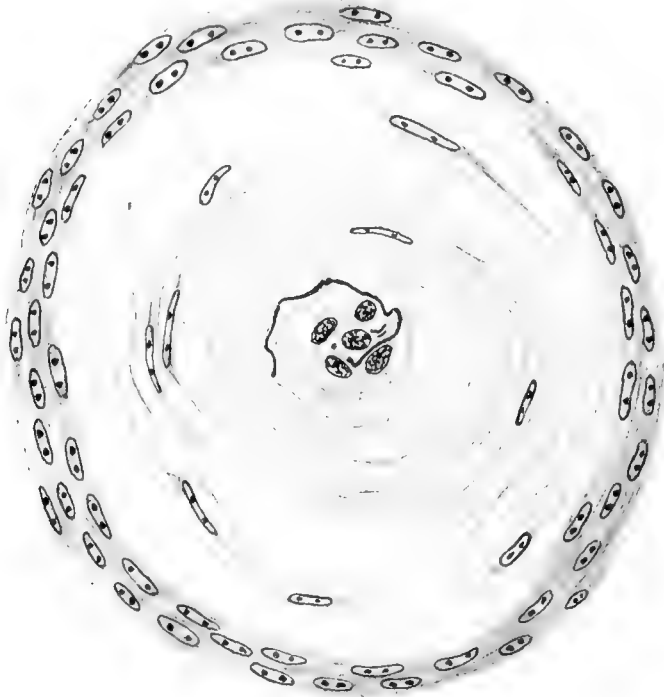


Fig. 5.

Transverse section of a HERBST-corpusele, with a nerve-thread that not only branches out in the protoplasm of the cells of the core, but proceeds from there into the connective-tissue lamellae round the inner core, where it continues its growth. 42 days after the cutting of the nerve.

These lamellae are connected by means of cellular processes, thus forming a whole.

Now in watching the regeneration it may be repeatedly observed that the nerve-thread, which has passed into the inner core of a HERBST-corpusele and ramifies in the protoplasm of the core, does not remain enclosed here in its entirety, but that some of the end-branches leave the core and intrude into the tissue of the connective-tissue lamellae. This then is the very place to see quite clearly,

that these nerve-fibers do not force their way into the lacunae between the connective-tissue lamellae, but that they lie in the lamellae, enveloped by protoplasm, and remain there. This envelop must decidedly partake of the nature of connective tissue. This observation, therefore, is in perfect harmony with what could previously be established for the neuromuscular spindle of striated muscles. In them also the in-growing regenerating nerve-threads could be seen moving through the protoplasm of the connective-tissue cells of the capsular space, which cells have developed into a conductive-tissue.

Utrecht, August 1922.

Chemistry. — “*Heterogeneous catalysis and the orientation of adsorbed molecules*”. By Prof. H. R. KRUYT and C. F. VAN DUIN.

(Communicated at the meeting of September 30, 1922).

In a previous communication¹⁾ we published investigations on the relation between the adsorption of reacting substances and the velocity of the reaction, with the object of coming to a better understanding of heterogeneous catalysis. In these investigations we found, that by giving coal to the reacting system a decrease of the velocity sets in, even in cases, where undoubtedly an increase of the reacting components in the surface layer takes place.

In accordance with the theory of I. LANGMUIR²⁾ and W. D. HARKINS³⁾ concerning the special condition of molecules, which are situated in surface layers, we tried to explain our results by the assumption 1. that adsorbed molecules have partly lost their mobility and consequently a great deal of the possibility of meeting and reacting with other molecules, and 2. that adsorption can cause positive catalysis only in the case, when the molecules are adsorbed in such a way that the number of effective collisions increases.

That adsorption in itself can have a decreasing effect was found when studying a monomolecular reaction, viz. the transformation of racemic dibromo-succinic acid into bromo fumaric acid and HBr⁴⁾. The results are given in the tables I and II.

Evidently a marked decrease in the velocity occurs.

We discussed in the paper cited above, that a positive contact catalysis can be expected only in the case, when the reacting group is turned away from the adsorbent and towards the surrounding liquid. With charcoal as an adsorbent, and water as milieu, all electrically polar groups will be turned towards the water; we therefore had chosen the reaction of $\alpha\beta$ dibromo-propionic acid and KJ (formation of acrylic acid, KBr and J₂). As might have been

1) Rec. trav. chim. Pays Bas 40, 249 (1921).

2) Journ. amer. chem. Soc. 39, 354 en 541 (1917).

3) Journ. amer. chem. Soc. 38, 2221 (1916) and 39, 1848 (1917).

4) Cf. HOLMBERG, Journ. f. prakt. Chem. 84, 145 (1911) and Zeitschr. f. physik. Chem. 79, 147 (1912).

TABLE I. *Without coal.*

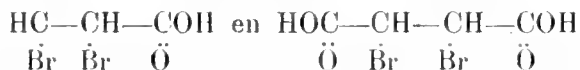
| Time in min. | c.c. NaOH $\frac{1}{20}n$ p. 10 cc. | conc. in $\frac{n}{400}$ | k mono-mol. |
|--------------|-------------------------------------|--------------------------|---------------|
| 0 | 20.22 | 19.98 | — |
| 1371 | 21.53 | 17.36 | 0.000103 |
| 2991 | 22.70 | 15.02 | 095 |
| 4288 | 23.57 | 13.28 | 095 |
| 6771 | 24.88 | 10.66 | 093 |

TABLE II. *With coal.*

| Time in min. | c.c. NaOH $\frac{1}{20}n$ p. 10 cc. not corr. | c.c. NaOH $\frac{1}{20}n$ p. 10 cc. corr. | conc. in $\frac{n}{400}$ | k mono-mol. |
|--------------|---|---|--------------------------|---------------|
| 0 | 18.91 | 20.22 | 19.98 | — |
| 1372 | 19.89 | 21.20 | 18.02 | 0.000075 |
| 2992 | 20.87 | 22.18 | 16.06 | 73 |
| 4311 | 21.29 | 22.60 | 15.22 | 63 |
| 6788 | 22.12 | 23.43 | 13.56 | 57 |

expected, we then have found and acceleration of the reaction. We repeated these experiments in a CO_2 -atmosphere and in the dark room to avoid complications. The result was almost the same: without coal we found $k = 0.000123$ and when coal was added $k = 0.000149$.

The place of the polar groups in dibromo-propionic acid is however not symmetric; the possibility remains that the COOH -group exerts a more vigorous orientating influence than the Br groups and consequently the latter will not be in a most favourable condition. A better result could be expected therefore in the case of the reaction of dibromo-succinic acid and KJ. A comparison between the formulae



will elucidate this immediately. Moreover, the stereochemical configuration suggests a still better arrangement in the case of the mesoform than in that of the racemic. In the tables III and IV we give the results obtained with the racemic, in the tables V and VI

TABLE III.
Racemic-acid *without coal.*

| Time in min. | c.c. thio $\frac{n}{40}$ | conc. $\frac{n}{800}$ | k mono-mol. |
|--------------|--------------------------|-----------------------|---------------|
| 0 | 0.08 | 19.92 | — |
| 790 | 1.82 | 18.18 | 0.000116 |
| 1392 | 2.99 | 17.01 | 113 |

k mean 0.000115

TABLE IV.
Racemic-acid *with coal.*

| Time in min. | c.c. J $\frac{n}{40}$ not corr. | c.c. J $\frac{n}{40}$ corr. | conc. $\frac{n}{800}$ | k mono-mol. |
|--------------|---------------------------------|-----------------------------|-----------------------|---------------|
| 0 | 17.27 | 20.12 | 19.92 | — |
| 776 | 11.72 | 14.57 | 14.37 | 0.000421 |
| 1380 | 8.90 | 11.75 | 11.55 | 395 |

k mean 0.000408

TABLE V.
Meso-acid *without* coal.

| Time in min. | c.c. thio $\frac{n}{40}$ | conc. $\frac{n}{800}$ | k mono- mol. |
|--------------------|-----------------------------|--------------------------|----------------------|
| 0 | 0.06 | 19.94 | — |
| 289 | 1.11 | 18.89 | 0.000187 |
| 576 | 2.12 | 17.88 | 189 |
| 806 | 2.83 | 17.17 | 186 |

k mean 0.000187

TABLE VI.
Meso-acid *with* coal.

| Time in min. | c.c. J $\frac{n}{40}$ not corr. | c.c. J $\frac{n}{40}$ corr. | conc. $\frac{n}{800}$ | k mono- mol. |
|--------------------|------------------------------------|--------------------------------|--------------------------|----------------------|
| 0 | 18.21 | 20.14 | 19.94 | — |
| 292 | 14.45 | 16.38 | 16.18 | 0.000716 |
| 582 | 11.20 | 13.13 | 12.93 | 744 |
| 809 | 9.47 | 11.40 | 11.20 | 713 |

k mean 0.000724

hose with the meso-acid. The initial concentration of the acid was $\frac{1}{40}$ n., that of KJ 2n.; work is done at 25° centigrade, in CO₂-atmosphere, in the dark room; 1 gramm of coal was added per 100 ccm.; in the experiments with coal 10 ccm. of the reacting mixture were poured into 20 ccm. of thio-solution of 0.02525 n.; the titration was done with a J-solution of $\frac{1}{40}$ n.

These results, shewing a great acceleration of the reactions, fully support our theory.

We have still other experience, which is in accordance with this theory. Dr. C. F. VAN DUIN wil give presently a detailed paper in *Recueil des Travaux chimiques des Pays Bas*.

Utrecht, VAN 'T HOFF-laboratory,
St. Andrews, United College of St. Leonards
and St. Salvador 1922.

Geology. — “*Fractures and Faults near the Surface of Moving Geanticlines. II. Abnormal Strikes near the Bending-points of the horizontal projection of the Geanticlinal axis.*” By Prof. H. A. BROUWER.

(Communicated at the meeting of September 30, 1922).

In a previous paper¹⁾ we have pointed to the occurrence of considerable transverse fractures near the bending points of the horizontal projection of the geanticlinal axis, which phenomenon has been explained by velocity differences on either side of these bending points.

Another phenomenon that may be observed near the bending points is the occurrence of older strikes, inclined or normal to the horizontal projection of the axis²⁾. This may be seen in rows of islands if the strikes in some islands do not coincide with the main trend of the islands. It is of great interest for determining the precise movements of the rows of islands, as will be shown in the following discussion.

The row of Islands Sermata-Islands, Babber, Tenimber-Islands.

In the islands Letti, Moa, Luang and Sermata the principal strikes are sometimes more or less parallel to the direction of the row, e.g. in Letti.

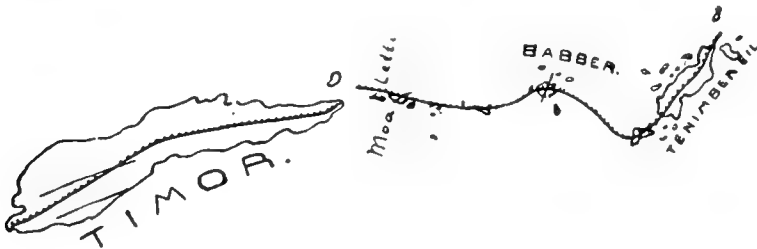


Fig. 1.

----- Horizontal projection of the geanticlinal axis (schematic representation).
 ——— Older strikes and coastlines.

In Moa some strikes are N.N.E. to N.E., so these are different from the direction of the row; in Luang the permian strata are

¹⁾ These Proceedings XXIII, p. 570,

²⁾ H. A. BROUWER, The horizontal movement of geanticlines and the fractures near their surface. Journ. of Geology. XXIX, 1921, p. 560—577.

intensely folded, with strong differences in strike and dip. If we construct the geanticlinal axis, as is generally done, with right angled bends, near Babber and near the southmost island Selaru of the Tenimber-Islands, so that the geanticlinal axis between these two islands is below the surface of the sea, the Tertiary strike in Babber (N.N.E.) is *about normal to the direction of the row.*

The connection of Halmaheira with the Pelew Islands.

The soundings between these islands do not go against the assumption that the prolongation of the Northern Peninsula of Halmaheira via Morotai towards the Helena-reef has a more or less east-western direction and bends in a more or less north-eastern direction towards the Pelew Islands. Even if considerable depths

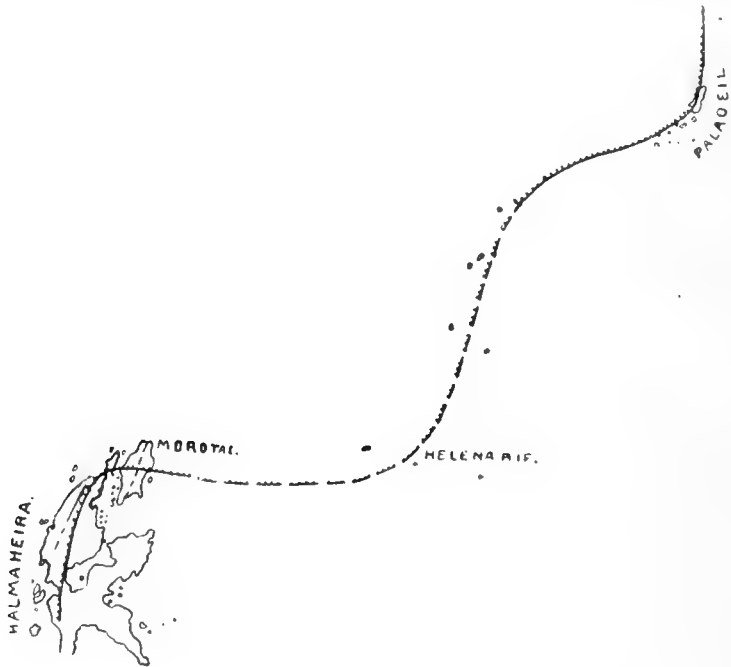


Fig. 2.

----- Horizontal projection of the geanticlinal axis (partly hypothetical).
 ——— Older strikes and coast-lines.

should exist where the E-W. prolongation of Halmaheira's northern peninsula is supposed to be, these depths may be the result of gaping fractures, that may exist near the bending-point. The known strikes on Morotai are in the direction of the longer axis of the island and are oblique to the supposed direction of the geanticlinal axis. This conception renders the resemblance between the outlines of Celebes

and Halmabeira more complete. The difference between them consists chiefly in the eastern part of the northern peninsula of Halmabeira being covered by the sea.

The row Formosa—Riukiu-Islands.

The prolongation of the Sakishima-group is generally considered to be linked to North-Formosa¹⁾, also by authors whose interpretation of the known facts differs from the one that will be put forward

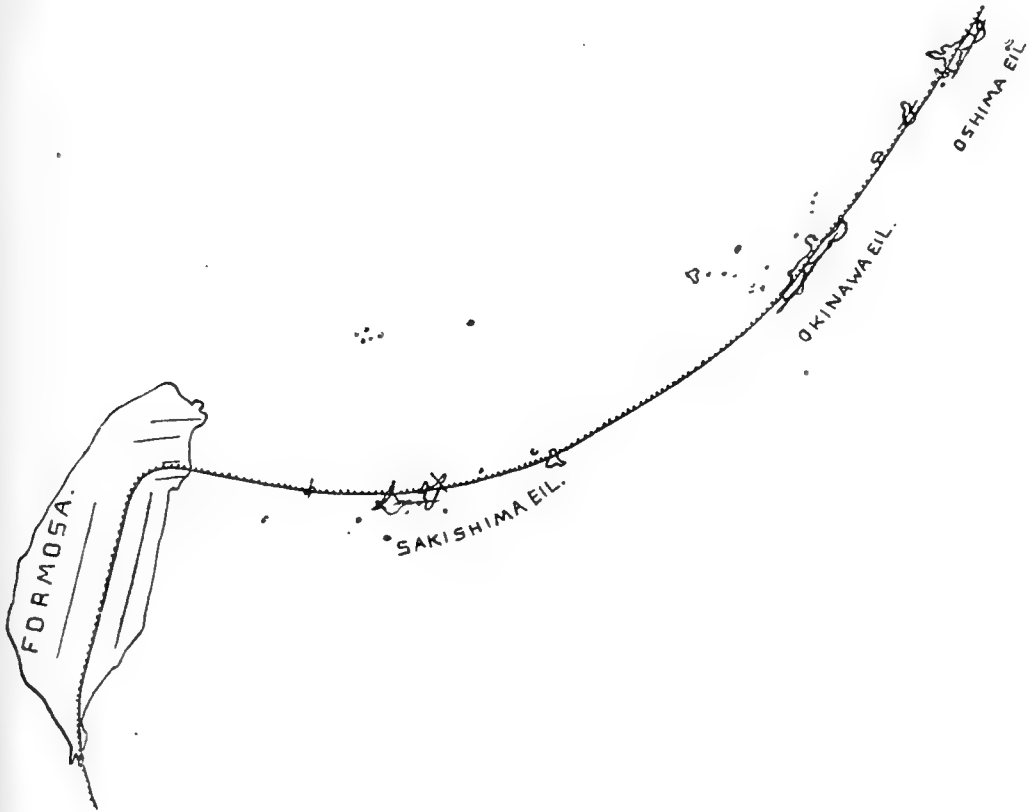


Fig. 3.

Explanation of Fig. 2.

lower down. The older strikes in the major part of Formosa are N.N.E. approximately parallel to the longer axis of the island. In North Formosa, however, their trend is about E—W, and they are cut off by the eastern coastline. In the Sakishima-group of the Riukiu-islands the strikes are irregular and are oblique or normal to the trend of the row of islands, while in the major part of the Riukiu

¹⁾ S. YOSHIWARA, Geologic structure of the Riukiu Curve etc. Journ. Coll. of Science, Tokyo. XVI. Part I, 1901.

Islands as far as Kiusjin the strikes are again about parallel to the direction of the row. This example seems to be similar to the two preceding ones, but the areas near Babber, as well as those near Morotai, from which this analogy might appear, are covered by the sea. In Formosa the bending of the older strikes is visible and moreover it can be seen that locally *near the bending point of the horizontal projection of the geanticlinal axis the older strikes are normal, or approximately so, to this projection, while on either side they are parallel to it.*

The movement at the surface of horizontally moving geanticlines.

In another publication we have already pointed to the difference in speed and direction of the movements at different depths¹⁾. The points, which were originally on the same vertical line, will in a later stage form an irregular curve in space. If the rate of movement has a vertical component, the vertical movement near the surface will be influenced by the vertical movement at greater depth.

The complicated horizontal and vertical movements, which differ already at a comparatively short distance, will cause new portions of the surface to form the crests of the moving geanticline. The direction of the older strikes with regard to the new geanticlinal axis in a subsequent phase of the movement, will depend upon the rate of movement at greater depth and that near the surface and upon the rate of erosion.

If the forces, which cause the movement of a geanticline, of which the highest parts rise above the sea-level as rows of islands, are deep-seated, the vertical movements will cause the uplift or subsidence of the islands, while the rate of horizontal movement at greater depth may differ considerably from the rate near the surface. We distinguish two extreme types of movement: 1° The horizontal movement near the surface is equal to zero. 2° The horizontal movement near the surface is similar to the movement at greater depth. In general neither of the extreme types will occur. In the first case no horizontal fracture-movements will take place at the surface, and straits generally correspond with a depression, islands with a culmination of the geanticlinal axis in a given stage of the movement.

In the second case the islands as such move in a horizontal direc-

¹⁾ H. A. BROUWER, The horizontal movement etc. loc. cit.
Id. The major tectonic features of the Dutch East Indies. Journ. Wash. Acad. of Sciences, 1922, p. 172—185.

tion, and straits may originate near the fractures without a subsidence of the geanticline along the axis. The movements near the surface are not equal to those at greater depth. But we suppose an extreme case, in which, considering broadly, the portions near the surface move at the same rate as those at greater depth.

The vertical movement and the effect of erosion.

Considering that during the movement erosion will continuously be at work in the portions above the sealevel, it will generally be possible to compare in the terminal phase the direction of the geanticlinal axis with the direction of the exposed older strikes. In case of a brief and not very intensive erosion, the tectonic details of a more plastic deformation at greater depths, are still invisible. The intensity of erosion decreases if, as in many rows of islands, the deformation of the geanticline takes place near the surface of the sea, and it is especially, when the vertical component of the rate of movement is great, that the tectonic details, which have been formed by a more plastic deformation at greater depth will soon be visible.

Rectilinear old strikes and curved geanticlinal axis with a bending-point in the last phase of movement under consideration.

The two extreme cases, mentioned above are :

1. *No horizontal movement at the surface.*

In the case represented by fig. 4 the old strikes cut the geanticlinal axes of the terminal phase on either side of the bending-point of $A'B'$ at an angle of about 45° , while nearer to A' and B' the older strike will gradually coincide with the new geanticlinal axis. If we assume that in the portions AC and DB , the movement has

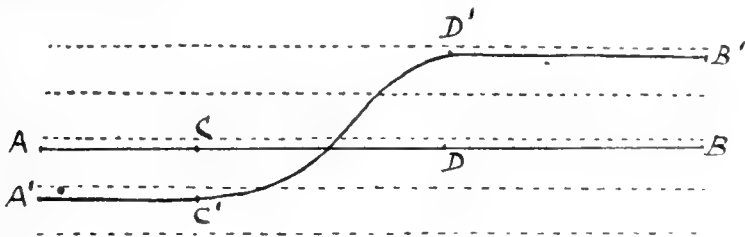


Fig. 4.

----- Older strike.

$A C B$ = horizontal projection of the geanticlinal axis in the initial stage of the movement under consideration.

$A' C' D' B'$ = *Ibid.* in the last phase of the movement under consideration.

taken place without velocity-differences and normal to the geanticlinal axis, gaping fractures will nevertheless be lacking in the portion $C'D'$, and in the case of a row of islands a strait will correspond with a minimum of the vertical projection of the geanticlinal axis.

2. *Horizontal movement at the surface, corresponding with the movement at greater depth.* In the portion $C'D'$ gaping fractures will be formed which — in so far as they occur near the surface of the sea — may be visible as straits between the islands.

In the positions $A'C'$ and $B'D'$ the old strikes will not differ from the direction of the new geanticlinal axis; to what extent they will do so in the portion $C'D'$, will depend on the movements near the surface. If these movements are non-rotational, differences up to 45° will occur; with rotation of the portions of the fractured surface the differences may be approximately zero.

Curving older strikes with a bending-point, and curving geanticlinal axis with displaced bending-point in the final stage.

One of the numerous variations of this more general case is represented in Fig. 5.

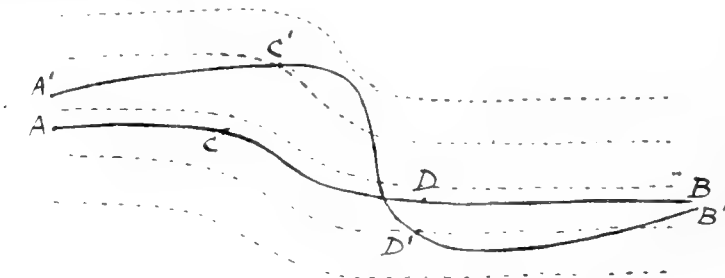


Fig 5.

----- = Older strike.

$A C D B$ and $A' C' D' B'$ = horizontal projection of the geanticlinal axis, resp. in the initial-, and the terminal stage of the period under consideration.

1. *No horizontal movement at the surface.* In the final stage the old strikes are nearly all oblique to the geanticlinal axis, near the bending-point even approximately normal to it. Straits will correspond with depressions of the geanticlinal axis. If the geological structure changes chiefly in the direction vertical to the old strike, islands of highly different structure will in some places be located side by side.

2. *Horizontal movement at the surface corresponding with that at greater depth.* When, in the terminal stage of the considered period of movement, the points A , B , C and D have reached respectively

A' , B' , C' and D' , gaping fractures will appear all along the line $A' C' D' B'$, which may have helped to form straits. If during their displacement the parts near the surface had at the same time rotating movements, the angles between the old strikes and the geanticlinal axis may approach zero in the final stage.

Explanation of the abnormal strikes near the bending-points.

The abnormal strike of the island of Babber (fig. 1) may be accounted for by assuming that the deformation of the geanticline at greater depth has been attended with similar horizontal movements near the surface, so that e.g. the geanticlinal portion near the surface of the Tenimber Islands may originally have been situated N.N.E. of Babber, while these parts have since been displaced considerably relative to each other in a horizontal direction.

When assuming that no horizontal movement has taken place near the surface, the abnormal strike in Babber may also have originated from the great velocity-differences in a horizontal direction at greater depth, with this difference that the submarine geanticlinal part between Babber and the Tenimber-Islands is not disrupted near the surface. If the bending-point is the horizontal projection of a point that gives a minimum in the vertical projection, it may be that near it a large part of the geanticlinal axis is below the sea. In that case data will be lacking for a comparison of the present morphology with the older tectonic structure of the parts on either side of the bending-point.

Likewise the connection of Halmaheira with the Pelew-Islands is covered by the sea in a considerably area on either side of the bending-point, but in Morotai, where the older strike is oblique to the geanticlinal axis, the geanticline still emerges from the sea, while here the resemblance of the coastline to that of the neighbouring part of Halmaheira points to horizontal movements of the islands as such. In the row Formosa-Riukiu Islands (Fig. 3), unlike in the preceding instances, the bend of the older strikes is not covered by the sea, which facilitates a more correct explanation of the phenomenon. The dips in the older formations of the Taiwan-mountains in Formosa point to WNW. movements, those in North-Formosa to southward movements, those in the major part of the Riukiu-Islands to S—E movements. It is evident therefore, that already during the older phases of the orogenetic process, there was a tendency to form a bending-point between Formosa and the Riukiu-Islands. Similar movements during the youngest phase of the mountain-building process gave origin to numerous fractures, e.g. those which

cut off the E- W strikes of North-Formosa at a right angle and separate the Sakishima Islands from each other and from Formosa.

According to our conception of the differences in character and rate of movement at different depths, the absence of islands between Formosa and the Sakishima Islands may be looked upon as resulting from the formation of gaping fractures, in connection with the velocity-differences in a horizontal direction at the surface near the bending-point, and from a minimum elevation of the geanticline near the bending-point of the horizontal projection of the axis. The abnormal strikes of the Sakishima-Islands find an explanation in the assumption of movements, such as have been referred to above in the discussion of a geanticlinal movement with curving older strikes and with a displaced bending-point in the final stage (Fig. 5). The movement can be described only in broad outlines, the details cannot be derived from the visible facts. Thus the strikes on the Sakishima-Islands have no constant direction, and differences occur between the strikes of the older and those of the more recent deposits. Near the bending-point, however, irregular movements can be expected, while at the same time the rate of vertical movement, and consequently the rate of erosion must in a high degree have influenced the present-day tectonic structure.

The abnormal strikes of the Sakishima-Islands have been explained differently by VON RICHTHOFEN¹⁾, who speaks of transverse subsidence causing an abnormal dip of the strata in connection with his explanation of the origin of the mountain arcs of Eastern Asia by tensional and not by compressional stress. In contradistinction to this interpretation by *vertical* movements, we have compared the features with those of other belts of islands and find an explanation of the abnormal strikes near the bending-points of the geanticlinal axis in considerable *horizontal movements*, which have already been discussed by us for various geanticlines in connection with other features.

¹⁾ F. VON RICHTHOFEN, Geomorphologische Studien aus Ost-Asien, III. Sitz. Ber. Akad. d. Wiss. Berlin. Phys.-math. klasse. 1902, p. 944 et seq.

Chemistry. — "*Cyclic Derivatives of Mannitol*". By Prof. P. VAN ROMBURGH and J. H. N. VAN DER BURG.

(Communicated at the meeting of October 28, 1922).

Many years ago the researches on the decomposition of the formates of polyhydric alcohols, and also those on the 1.3.5. hexatriene, induced one of us (v. R.) in collaboration with Mr. VAN MAANEN, to study the action of formic acid on mannitol.¹⁾

After they had succeeded in preparing the hexaformate of mannitol it appeared against expectation that on being heated this substance yielded no hexatriene or only traces of it; on the other hand it yielded a product of the formula C_6H_8O , though in small quantities. This product, which boiled at $107-109^\circ$, had already been obtained by FAUCONNIER²⁾, together with isomannide, on heating mannitol with formic acid.

Also the tetraformate of mannitane and the diformate of isomannide were obtained by heating mannitol and formic acid, both in pure state. FAUCONNIER³⁾ found already, that by heating the diformate of isomannide only carbon oxide was evolved, with formation of isomannide; when on the other hand the former was heated, carbonic acid gas was formed, and again the oxide C_6H_8O was obtained.

The following constants were found for this latter product, which is very strongly levo-rotatory. Bp. 107° , $d_{15}^{15} = 0,9226$, $n_{D,15} = 1,3567$. With bromine it gives a liquid dibromide, $C_6H_8Br_2O$, $d_{15}^{17,5} = 0,8622$, Bp. 15 mm. $118^\circ.5$. A tetrabromide could not be obtained.

Reduction with hydrogen, according to SABATIER and SENDERENS, gave with C_6H_8O , both at 110° and at 180° a product of the formula $C_6H_{10}O$, which did not boil constantly under ordinary pressure but at 16° at 23 mm. Hence only 1 mol. of hydrogen had been absorbed.

In virtue of the decomposition of the di-formate of isomannide, in which only carbon oxide is formed, (so that it may be assumed not to

¹⁾ VAN MAANEN, Diss. Utrecht, 1909.

²⁾ C. r. 100, 914 (1885).

³⁾ Bull. Soc. Chim. N.S. 41, 125 (1884).

contain two vicinal OH-groups) VAN ROMBURGH and VAN MAANEN

proposed among others the formula $\text{CH}_2 \cdot \overset{\text{OH}}{\underset{|}{\text{CH}}} \cdot \overset{\text{O}}{\text{CH}} \cdot \overset{\text{O}}{\text{CH}} \cdot \text{CH}_2$, for

isomannide, and $\text{CH}_2 \cdot \overset{\text{O}}{\text{CH}} \cdot \overset{\text{OH}}{\underset{|}{\text{CH}}} \cdot \overset{\text{OH}}{\underset{|}{\text{CH}}} \cdot \text{CH}_2 \cdot \text{OH}$

for mannitane, the formate of which gave only carbon dioxide.

The compound $\text{C}_6\text{H}_8\text{O}$ might therefore be represented by the formula $\text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH} \cdot \text{CH} : \text{CH}_2$, hence it would be α -vinylidihydrofurane.

In 1917 WINDAUS and TOMICH¹⁾ too studied the compound $\text{C}_6\text{H}_8\text{O}$, and could obtain by its reduction with hydrogen under the influence of palladium, an addition of two mol. of hydrogen, so that $\text{C}_6\text{H}_{12}\text{O}$ was formed, which substance according to them should be identical with a δ -hexylène oxide described by LIPP²⁾, in which not a 5-ring, but a 6-ring occurs: $\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}-\text{CH}_2$, so that the

original oxide would have the formula $\text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CH} \cdot \text{CH}_2$.

They concluded to the identity of the two saturated oxides by the equality of the boiling-point, both of the oxides and of the dibromides derived from them. WINDAUS rejects the possibility of the oxide being a furane-derivative, because then no asymmetric formula would be possible. This argument is, however, not valid with regard to the formula drawn up above.

It has appeared from investigations on the action of ozone on the oxide $\text{C}_6\text{H}_8\text{O}$, undertaken by Mr. BRUINS in the Utrecht Laboratory after the publishing of WINDAUS and TOMICH's paper, that in this reaction only carbonic acid, formaldehyde, and formic acid could be found, but no products in which a CH_2 -group occurs, which pleads against WINDAUS's formula. This, however, did not give a rigorous proof for the α -vinylidihydrofurane-formula. To obtain perfect certainty, we have followed another course.

First of all by reduction of $\text{C}_6\text{H}_8\text{O}$ with hydrogen of a pressure of two atmospheres in the presence of palladiumsol the saturated

¹⁾ Göttinger Nachrichte Math. Phys. Kl. 1917, S. 462.

²⁾ B. 18, 3275 (1885).

oxide $C_6H_{11}O$ was prepared. We used for this purpose an apparatus as indicated by SKITA¹⁾, in which the process of the reaction can be easily followed. During the fractionation the substance polymerizes partially, so that a perfectly pure product only can be obtained at the expense of considerable loss.

In spite of careful purification the possibility exists therefore that a small quantity of unsaturated product is left behind.

The substance was optically inactive, and showed the following constants:

$$\text{bp. } 103^{\circ}_x\text{—}106^{\circ} \quad d_{16}^{16} 0.8693 \quad n_D 1.42797$$

(analysis: found C 71.8 H 12.3; calc. C 72.0 H 12.0).

In the way indicated by LIPP loc. cit. we have further prepared the δ -hexylene oxide, with the following constants:

$$\text{bp}_{767} 106^{\circ}\text{—}106^{\circ}.2, \quad d_{16}^{16} 0.8617, \quad n_D 1.41887.$$

Since on reduction α -vinyl-dihydrofuran must yield γ -hexylene oxide, we have also prepared this oxide according to WOHLGEMUTH²⁾, who however, only gives its boiling-point, viz. $106^{\circ}\text{—}108^{\circ}$ at 770 mm.

The following constants were found: $Bp_{760} 106^{\circ}.5\text{—}107^{\circ}$, $d_{16}^{16} 0.8609$, $n_D 1.41685$.

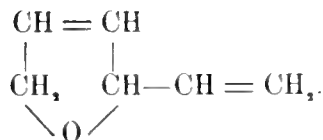
The corresponding bromides were obtained by treatment of these oxides with the 8-10-fold volume of hydrobromic acid (48 %) in a sealed tube for 1 to 2 hours at 100° . The 1-5-dibromo hexane boiled at 15 mm. at $105^{\circ}\text{—}108^{\circ}$ (analysis found Br. 65.3 %, calc. 65.5), the 1-4-dibromo hexane at $106^{\circ}\text{—}108^{\circ}$ at 15 mm. (Br. found 65.4). The boiling-point of the di-bromide obtained from the reduced oxide $C_6H_{11}O$ was $106^{\circ}\text{—}110^{\circ}$ at 14 mm. (Br. found 65.6). It is evident that from the equation of the physical constants, both of the oxides and of their di-bromides, no conclusion can be drawn about the structure of the reduced oxide $C_6H_{11}O$, unless there are large quantities of the substances at our disposal. It was, therefore, necessary to try to obtain crystallized compounds. An attempt to prepare crystallized benzoates of the glycols corresponding with the dibromides did not meet with success. The action of piperidine on the di-bromides, on the other hand, in which quaternary ammonium bromides were formed, had a favourable result.

In analogy with VON BRAUN³⁾, who made act 1-5-dibromo pentane

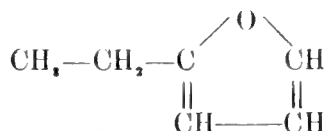
¹⁾ B. **45**, 3595 (1912).

²⁾ C.r. **159**, 80 (1914).

³⁾ B. **39**, 4347 (1906).



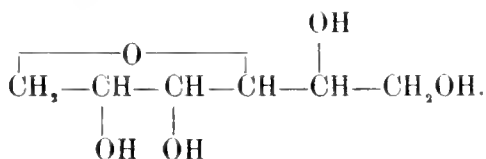
The place of the double bonds in this compound is now exactly known. The substance being optically active, an asymmetric carbon atom must be present in it; a formula, e. g. as the following:



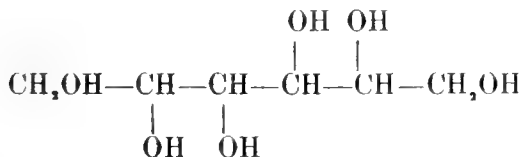
would not satisfy, as has also been remarked by WINDAUS.

As α -vinylidihydrofuran is formed from mannitan tetra formate, it is now possible to draw up a structure formula for the anhydrides of mannitol, viz. mannitan and isomannide.

We then arrive at the following scheme for mannitan:



In connection with the spatial formula of mannitol:

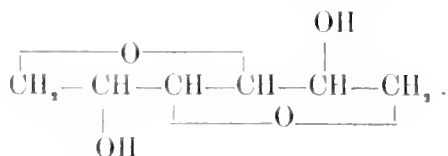


We see that as soon as the oxide-ring is formed between the C-atoms 1 and 4, the OH-groups at 2 and 3 will be at the same side. Besides the molecule contains two OH-groups situated beside each other at 5 and 6 (in perfect accordance with the pyrogenic decomposition of the tetra-formate, in which formic acid and carbon dioxide are split off from OH-groups placed beside each other), so that here a possibility must be for the formation of a di-acetone compound. In fact this compound was obtained as a colourless substance crystallizing in glossy leaflets, melting-point 155° analysis C 58.83, H 8.38; calculated C 59.0 H 8.2).

The conductivity of boric acid will also be increased greatly by mannitan. ¹⁾

¹⁾ BÖESEKEN, Rec. 40, 553 (1921).

Through the formation of a second oxide ring, we then arrive at the following formula for the second anhydride



The places of the OH-groups here are at 2.5; hence no acetone derivative can be formed, nor will the conductivity of boric acid be raised. On treatment with acetone and 1% hydrochloric acid the isomannide was actually recovered. The results of the measurements of the conductivity are recorded in the following table:

| Capacity of the vessel 0.4106. | | | | | | | |
|---|----------|------|----------------------|--------------------|-------|----------------------|-----------------------|
| Conductivity of the boric acid 0.5 mol. Litre $30 \times 10^{-6} = K_3$. | | | | | | | |
| | In water | | | In boric acid sol. | | | $K_1 - (K_2 + K_3)$. |
| | A. | W. | $K_2 \times 10^{-6}$ | A. | W. | $K_1 \times 10^{-6}$ | |
| Mannitol | 500 | 5660 | 72.5 | 500 | 1037 | 396 | 294 |
| Mannitane | 500 | 3240 | 126.8 | 500 | 440 | 933 | 776 |
| Isomannide | | | | 480 | 11000 | 34.4 | 4.4 |

The concentrations were 0,2 mol./Litre.

After deduction of the conductivity for water 3×10^{-6} , we find therefore that iso-mannide in a very small, quite negligible degree increases the conductivity, whereas this increase for mannitane exceeds that of mannitol more than 2½ times.

Of the forgoing we may conclude that the structure of the unsaturated oxide C_6H_8O is proved, likewise that of mannitane. The given formula for isomannide seems to be exceedingly probable.

Utrecht, Org. Chem. Labor. of the University.

Chemistry. — “*In-, mono- and divariant equilibria*”, XXII. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of October 28, 1922).

Equilibria of n components in n + 1 phases, when the quantity of one of the components approaches to zero. The influence of a new substance on an invariant equilibrium.

For the equilibrium:

$$E = F_1 + F_2 + \dots + F_{n+1} \dots \dots \dots (1)$$

of n components in $n + 1$ phases, as we have seen furtherly, are valid the equations:

$$Z_i - x_i \frac{\partial Z_i}{\partial x_i} - y_i \frac{\partial Z_i}{\partial y_i} - \dots = K \dots \dots \dots (2)$$

wherein

$$i = 1, 2, \dots (n + 1)$$

and further:

$$\left. \begin{aligned} \frac{\partial Z_1}{\partial x_1} = \frac{\partial Z_2}{\partial x_2} = \dots = \frac{\partial Z_{n+1}}{\partial x_{n+1}} = K_x \\ \frac{\partial Z_1}{\partial y_1} = \frac{\partial Z_2}{\partial y_2} = \dots = \frac{\partial Z_{n+1}}{\partial y_{n+1}} = K_y \end{aligned} \right\} \dots \dots \dots (3)$$

to which still must be added the corresponding equations for the variables $z_1 z_2 \dots u_1 u_2 \dots$ etc. As it is apparent from the number of equations (viz. $n^2 + n$) and the number of variables (viz. $n^2 + n + 1$), this equilibrium is monovariant, consequently, in the P, T -diagram we represent it by a curve, which we call E .

When in this equilibrium E all phases with constant composition contain together only $n-1$ of the n components, so that in these phases one of the components f.i. X is missing, then, in the phases with variable composition the quantity of this component X may approach to Zero.

Then the equilibrium E passes into an equilibrium, that we call $E(x=0)$ which consists of $n-1$ components in $n + 1$ phases and that, consequently is invariant; in the P, T -diagram it is represented therefore, by a point which we shall call $i(x=0)$. This point is the invariant terminating — or beginning — point of curve E .

As we do approach the quantity of the component X to zero, we put again:

$$Z_1 = Z'_1 + RTx_1 \log x_1 \quad Z_2 = Z'_2 + RTx_2 \log x_2 \quad . \quad (4)$$

etc. In similar way as we have done formerly, now we find:

$$H_i dT - V_i dP + RTx_i + y_i d\left(\frac{\partial Z'}{\partial y}\right)_i + \dots = -dK \quad . \quad (5)$$

$$i = 1, 2, \dots (n + 1)$$

$$x_2 = \mu_2 x_1 \quad x_3 = \mu_3 x_1 \dots x_{n+1} = \mu_{n+1} x_1 \quad . \quad . \quad (6)$$

$$d\frac{\partial Z'_1}{\partial y_1} = d\frac{\partial Z'_2}{\partial y_2} = \dots = d\frac{\partial Z'_{n+1}}{\partial y_{n+1}} = dK_y \quad . \quad . \quad (7)$$

To these equations (7) must be added the corresponding equations for the variables $z_1 z_2 \dots u_1 u_2$. The sign d indicates that there must be differentiated with respect to all variables.

Now we add to one another the $n+1$ equations (5) after having multiplied the first with λ_1 , the second with λ_2 , etc. Then we obtain:

$$\left. \begin{aligned} \Sigma (\lambda H) \cdot dT - \Sigma (\lambda V) \cdot dP + RT \Sigma (\lambda x) + \Sigma (\lambda y) dK_y + \\ + \Sigma (\lambda z) \cdot dK_z + \dots = - \Sigma (\lambda) \cdot dK \end{aligned} \right\} \quad (8)$$

Now we put:

$$\left. \begin{aligned} \Sigma (\lambda) = 0 \quad \text{of} \quad \lambda_1 + \lambda_2 + \dots + \lambda_{n+1} = 0 \\ \Sigma (\lambda x) = 0 \quad \text{of} \quad \lambda_1 x_1 + \lambda_2 x_2 + \dots + \lambda_{n+1} x_{n+1} = 0 \\ \Sigma (\lambda y) = 0 \quad \text{of} \quad \lambda_1 y_1 + \lambda_2 y_2 + \dots + \lambda_{n+1} y_{n+1} = 0 \end{aligned} \right\} \quad . \quad (9)$$

etc. but *not* $\Sigma (\lambda H)$ and $\Sigma (\lambda V)$.

Then we have n equations, so that that the n ratio's between $\lambda_1 \lambda_2 \dots \lambda_{n+1}$ are defined. The reaction:

$$\lambda_1 F_1 + \lambda_2 F_2 + \dots + \lambda_{n+1} F_{n+1} = 0 \quad . \quad . \quad (10)$$

which may occur in the monovariant equilibrium E , when the quantity of the component X is infinitely small, is, therefore, also defined. We shall call this equilibrium, which differs extremely little from $E(x=0)$ the equilibrium E ($\text{Lim } x=0$) or shortly the equilibrium $E(x)$. With the aid of (9) now (8) passes into:

$$\left(\frac{dP}{dT}\right)_x = \frac{\Sigma (\lambda H)}{\Sigma (\lambda V)} \quad . \quad . \quad . \quad (11)$$

wherein $\lambda_1 \lambda_2$ are defined by (9).

Consequently the direction of the tangent to curve E in its invariant point of beginning or terminating $i(x=0)$ is defined by (11). The relation (7) (XIX) is, therefore, true also when the quantity of one of the components approaches to zero.

phases is defined by (6). By (13) is defined whether the temperature is rising or falling; by (15) is defined whether the pressure is increasing or decreasing.

We write the isovolumetrical reaction:



wherein all reaction-coefficients have been taken positive. Now we have:

$$\Sigma (\lambda H)_V = \lambda_q H_q + \lambda_{q+1} H_{q+1} + \dots - \lambda_1 H_1 - \lambda_2 H_2 - \dots$$

$$\Sigma (\lambda x)_V = \lambda_q x_q + \lambda_{q+1} x_{q+1} + \dots - \lambda_1 x_1 - \lambda_2 x_2 - \dots$$

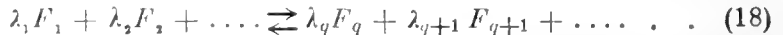
Now we assume that we have written reaction (17) in such a way that it proceeds on addition of heat from the left to the right; consequently $\Sigma (\lambda H)_V$ is positive. In order to determine the sign of $\Sigma (\lambda x)_V$ we have to dissolve $\lambda_1 \lambda_2 \dots$ from (12) and we must know the partition of the new substance between the different phases; this may be found from (6).

In some cases the sign of $\Sigma (\lambda x)_V$ is known, however, at once without this calculation. When f.i. the new substance occurs only in one or more of the phases, which arise in (17) on addition of heat, consequently in $F_q F_{q+1} \dots$, then is $x_1 = 0 \ x_2 = 0 \dots x_{q-1} = 0$ and, therefore $\Sigma (\lambda x)_V$ is positive. It follows then from (13) that $(dT)_x$ is negative.

When, however, the new substance occurs only in one or more of the phases, which arise in (17) on withdrawing heat, then $x_q x_{q+1} \dots$ are zero, so that $\Sigma (\lambda x)_V$ is negative. Then it follows from (13) that $(dT)_x$ is positive.

When, however, the new substance occurs in both groups of phases, then only a calculation more in detail may decide on the sign of $\Sigma (\lambda x)_V$ and consequently also on the sign of $(dT)_x$.

Now we represent the isentropical reaction also by



However we have to take in mind, that $\lambda_1 \lambda_2 \dots$ in this case, must not be dissolved from (12) but from (14). Consequently in (18) $\lambda_1 \lambda_2 \dots$ shall have not only other values than in (17), but one or more of them may have also other signs, so that they must be transferred from the one part to the other. Now we have:

$$\Sigma (\lambda V)_H = \lambda_q V_q + \lambda_{q+1} V_{q+1} + \dots - \lambda_1 V_1 - \lambda_2 V_2 - \dots$$

$$\Sigma (\lambda x)_H = \lambda_q x_q + \lambda_{q+1} x_{q+1} + \dots - \lambda_1 x_1 - \lambda_2 x_2 - \dots$$

Now we assume that reaction (18) is written in such a way that it is proceeding from left to right with increase of volume. Consequently $\Sigma (\lambda V)_H$ is positive. When the new substance occurs only

in one or more of the phases which arise at increase of volume, then $\Sigma(\lambda x)_H$ is positive and, in accordance with (15) therefore also $(dP)_x$.

When, however, the new substance occurs only in one or more of the phases which arise on decrease of volume, then $\Sigma(\lambda x)_H$ is negative and therefore, also $(dP)_x$ is negative.

Hence we may deduce the following rules:

When we add a new substance to an invariant equilibrium $E(x=0)$ then a monovariant equilibrium E occurs, which we represent in a P, T -diagram by a curve E ; when the new substance occurs only in one or more of the phases, which arise at the isovolumetrical reaction on addition (withdrawal) of heat, then the temperature is lowered (raised); consequently curve E proceeds starting from its invariant beginning-point towards higher (lower) pressures.

In some cases we may also deduce something on the direction of curve E in its invariant beginning-point in the following way. We assume that the new substance which is added to the invariant equilibrium:

$$E(x=0) = F_1 + F_2 + \dots + F_q + F_{q+1} + \dots + F_{n+1}$$

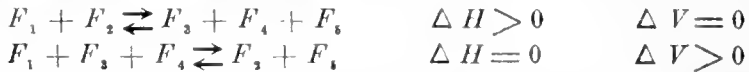
occurs only in the phases $F_{q+1} \dots F_{n+1}$ and, therefore, not in $F_1, F_2 \dots F_q$. This is surely the case when $F_1 \dots F_q$ are phases of constant composition. When we take away from the equilibrium E the phases $F_{q+1} \dots F_{n+1}$, then we keep an plurivariant equilibrium $F_1 \dots F_q$; this is represented in the P, T -diagram by a plurivariant region. As curve E must be situated in this region, hence follows the said-above. In the special case that the new substance occurs in one of the phases only, curve E coincides, therefore, with one of the monovariant equilibria of the equilibrium $E(x=0)$.

Before applying those considerations to some cases, firstly I will draw the attention to some points, which have been already discussed before. When we know of the isovolumetrical and isentropical reaction the ratio of the coefficients $\lambda_1, \lambda_2, \dots$ and also in which direction those reactions proceed on addition of heat or on increase of volume, then we shall say that those reactions are known quantitatively. When we know, however, only the signs of $\lambda_1, \lambda_2, \dots$ and also in which direction the reactions are proceeding on addition of heat or on increase of volume, then we shall say that the reactions are known qualitatively. Then we only know which phases are at the one side and which at the other side of the reaction-sign.

When we know of each phase of the invariant equilibrium $E(x=0)$ the entropy, the volume and the composition, then with the aid of (12) and (14) we may define the isovolumetrical and isentropical reaction quantitatively. Consequently we are able to draw exactly the direction of the different monovariant curves in the P, T -diagram, we call it a quantitative P, T -diagram.

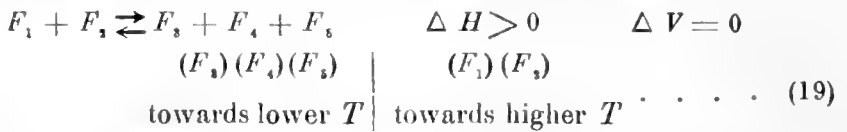
When we only know both reactions qualitatively, then we can define only whether the monovariant curves proceed, starting from the invariant point towards higher or lower temperatures and towards higher or lower pressures; but then their situation with respect to one another is still undefined; this we call a qualitative P, T -diagram.

We take for example the reactions:

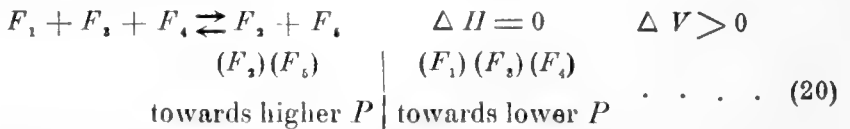


of a ternary invariant equilibrium. The first is, according to the supposition $\Delta V = 0$, the isovolumetrical reaction and it takes place, according to the supposition $\Delta H > 0$ from left to right on addition of heat. It appears from $\Delta H = 0$ and $\Delta V > 0$ that the second one is the isentropical reaction and that the volume increases from left to right.

In accordance to our former considerations, now we have:



Further we have:



In accordance to our previous notation, herein is:

$$(F_1) = F_2 + F_3 + F_4 + F_5, \quad (F_2) = F_1 + F_3 + F_4 + F_5, \text{ etc.}$$

Now we know qualitatively the P, T -diagram; we know viz. that from the invariant point curve (F_1) is going towards higher T and lower P ; curve (F_2) goes towards higher T and at the same time towards higher P , etc.

Inversely we can also find from a qualitative P, T -diagram the qualitative isovolumetrical and isentropical reaction. When we know f.i. that the curves (F_1) and (F_2) go towards higher temperatures and (F_3) (F_4) and (F_5) towards lower temperatures, then we have to construe (19) in the inverse direction viz. from the bottom to the top, in order to find the isovolumetrical reaction.

When we know that (F_2) and (F_3) go towards higher temperatures, and (F_1) , (F_2) and (F_3) towards lower pressures, then we find at once, by construing (20) in the inverse direction the isentropical reaction.

Firstly we shall apply those considerations to a simple case viz. to the addition of a new substance to the invariant unary equilibrium $E(x=0) = F + L + G$. The P, T -diagram may belong to two types, viz. when the volume decreases, on melting of the solid substance, then fig 1 is true; when the volume increases, then fig 2 is valid. The regions in which occur the phases F , L and G are indicated by the same letters, but in a circle; the curves are represented by (F) , (L) and (G) ; in accordance with our notation is $(F) = L + G$, etc.

When we add to $E(x=0)$ a new substance, which occurs only in the liquid, then the monovariant equilibrium $E = F + L + G$ arises; when we take away from it L , then we keep the equilibrium $F + G = (L)$.

Curve E coincides therefore in figs 1 and 2 with curve (L) of the invariant unary equilibrium $E(x=0)$.

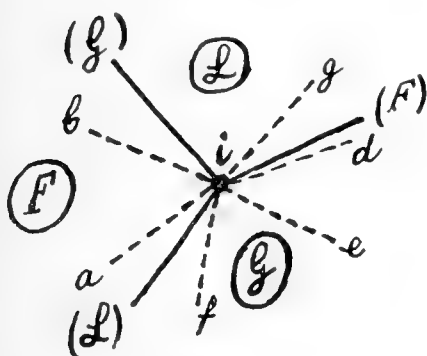


Fig. 1.

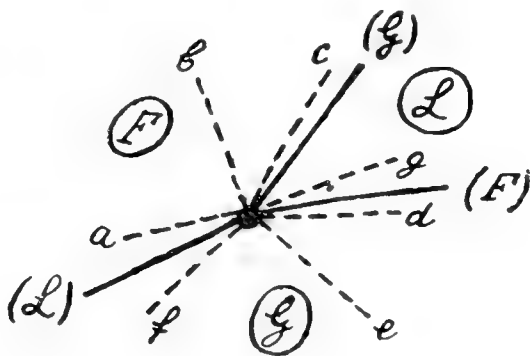


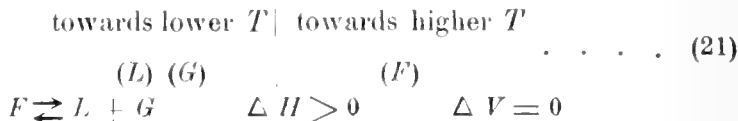
Fig. 2.

When we add a volatile substance, then we must take away from the monovariant equilibrium the phases L and G , so that we keep F only. Therefore, curve E must be situated in the region F , as f. i. ia , ib and ic in the figs 1 and 2.

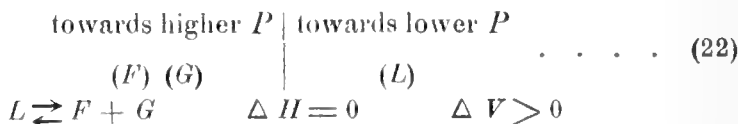
When we add a substance, which is not volatile, which gives, however, mixed-crystals with F , then we must take away from the equilibrium E the phases F and L , so that the vapour G only remains. Therefore, curve E must be situated in the region G .

We may obtain also these results by using the qualitative isovolumetrical and isentropical reaction, which we can deduce easily

from the figs 1 and 2. It follows from the position of the curves in fig 1.



and



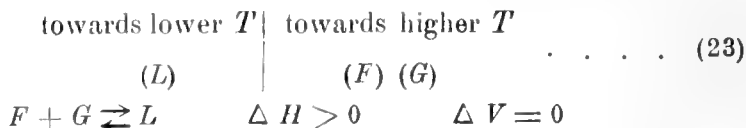
so that both reactions are known qualitatively.

Now we add to this equilibrium $E(x=0) = F + L + G$ a substance, which occurs in the liquid only. As in the isovolumetrical reaction (21) L is placed at the right side of the reaction-sign, consequently, in accordance with our rules, T is lowered; as in the isentropical reaction (22) L is placed at the left side of the reaction-sign, the pressure is also lowered, therefore.

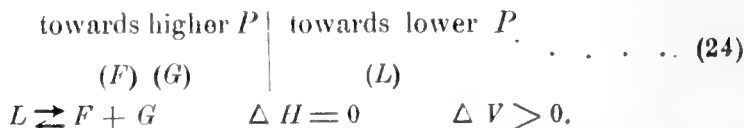
Consequently in fig. 1 curve E proceeds starting from point i towards lower T and P ; this is in accordance with the deduced above, that curve E coincides with curve (L) in this case.

When we add a volatile substance, than it occurs in L and G . As both those phases are placed in (21) at the right side of the reaction-sign, consequently T is lowered. As L and G are placed in (22) at different sides of the reaction-sign, the pressure may be as well increased as decreased. Therefore, curve E may be represented by ia or ib in fig. 1. Which of these curves may occur in a definite case, cannot be deduced in this manner; we are able to do this, as we shall see further, with the aid of the quantitative reactions.

In order to deduce the qualitative reactions from fig. 2, we write:



and



When we add a new substance, which occurs in L and G , then we find that curve E may be represented in fig. 2 by ia , ib or ic .

It is apparent from the previous that by simple considerations we may deduce already something about the direction of curve E from the qualitative P, T -diagram of an invariant equilibrium $E(x=0)$,

When, however, we know the quantitative reactions, then we are able to deduce not only the quantitative P, T -diagram for the equilibrium $E(x=0)$ but also $(dT)_x$ and $(dP)_x$ for the equilibrium E and consequently we can define exactly the direction of curve E .

When we represent entropy and volume of F by H and V , of L by H_1 and V_1 and of G by H_2 and V_2 , and when we assume that the substance melts on decrease of volume, then we have:

$$H_2 > H_1 > H \quad \text{and} \quad V_2 > V > V_1 \quad \dots \quad (25)$$

We write the isovolumetrical reaction:

$$F + \lambda_1 L + \lambda_2 G = 0 \quad \dots \quad (26)$$

As, in accordance with (12):

$$1 + \lambda_1 + \lambda_2 = 0 \quad \text{and} \quad V + \lambda_1 V_1 + \lambda_2 V_2 = 0 \quad \dots \quad (27)$$

it follows:

$$\lambda_1 = -\frac{V_2 - V}{V_2 - V_1} \quad \text{and} \quad \lambda_2 = -\frac{V - V_1}{V_2 - V_1} \quad \dots \quad (28)$$

so that λ_1 and λ_2 are both negative. Instead of (26) we now write:

$$F \rightleftharpoons \lambda_1 L + \lambda_2 G \quad \dots \quad (29)$$

wherein

$$\lambda_1 = \frac{V_1 - V}{V_2 - V_1} \quad \text{and} \quad \lambda_2 = \frac{V - V_1}{V_2 - V_1} \quad \dots \quad (30)$$

and

$$\Sigma (\lambda H)_T = \lambda_1 H_1 + \lambda_2 H_2 - H \quad \dots \quad (31)$$

Now we may prove that $\Sigma (\lambda H)_T$ is generally positive, so that, on addition of heat the isovolumetrical reaction (29) proceeds from left to right.

In a similar way we find for the isentropical reaction:

$$\mu_1 L \rightleftharpoons F + \mu_2 G \quad \dots \quad (32)$$

and

$$\Sigma (\lambda V)_H = V + \mu_1 V_1 - \mu_2 V_2$$

wherein

$$\mu_1 = \frac{H_1 - H}{H_2 - H_1} \quad \text{en} \quad \mu_2 = \frac{H_1 - H}{H_2 - H_1} \quad \dots \quad (33)$$

so that μ_1 and μ_2 are both positive.

As $\Sigma (\lambda V)_H$ is positive, reaction (32) proceeds from left to right with increase of volume.

With the aid of reactions (29) and (32), as is discussed in previous communications we now can deduce the P, T -diagram quantitatively; then we find fig. 1.

Now we add a new substance which occurs in the liquid only.

When we call its concentration x_1 , then we have:

$$\Sigma(\lambda x)_V = \lambda_1 x_1 \text{ and } \Sigma(\lambda x)_H = -\mu_1 x_1$$

so that, in accordance with (13) and (15):

$$(dT)_x = \frac{-RT\lambda_1 x_1}{\Sigma(\lambda H)_V} \text{ and } (dP)_x = \frac{-RT\mu_1 x_1}{\Sigma(\lambda V)_H} \quad \dots \quad (34)$$

Consequently in fig. 1 curve E proceeds, starting from point i towards lower P and T .

It follows from (33):

$$\left(\frac{dP}{dT}\right)_x = \frac{\mu_1}{\lambda_1} \cdot \frac{-H + \lambda_2 H_2 + \lambda_1 H_1}{V + \mu_2 V_2 - \mu_1 V_1} = \frac{H_2 - H}{V_2 - V} \quad \dots \quad (35)$$

Hence it appears that in fig. 1 curve E coincides with curve (L) . Also we may find (34) at once with the aid of (9) and (11). We put viz.:

$$\Sigma(\lambda) = 1 + \lambda_1 + \lambda_2 = 0 \text{ and } \Sigma(\lambda x) = \lambda_1 x_1 = 0$$

so that $\lambda_1 = 0$ and $\lambda_2 = -1$. Hence it follows:

$$\Sigma(\lambda H) = H - H_2 \text{ and } \Sigma(\lambda V) = V - V_2,$$

consequently for (11) the same value as in (34).

When the new substance occurs in liquid and vapour with the concentrations x_1 and x_2 , then we have:

$$\text{in accordance with (29):} \quad \Sigma(\lambda x)_V = \lambda_1 x_1 + \lambda_2 x_2,$$

$$\text{and in accordance with (32):} \quad \Sigma(\lambda x)_H = -\mu_1 x_1 + \mu_2 x_2,$$

so that $(dT)_x$ and $(dP)_x$ are known again. We see that $(dT)_x$ is negative, but that $(dP)_x$ may be as well positive as negative. Curve E , therefore, may be situated in fig. 1 as ia or ib .

When we put:

$$\frac{\mu_1}{\mu_2} = \frac{H_2 - H}{H_1 - H} = K \quad \dots \quad (36)$$

then is

$$\Sigma(\lambda x)_H = \mu_2 (x_2 - Kx_1) \quad \dots \quad (37)$$

wherein, in accordance to (35), $K > 1$.

Now we find:

for $\frac{x_2}{x_1} > K$ is $(dP)_x > 0$; consequently curve E goes, starting from point i towards higher pressures;

for $\frac{x_2}{x_1} < K$ is $(dP)_x < 0$; consequently curve E goes, starting from point i towards lower pressures.

When f.i. is $K=5$, then the concentration of the new substance in the vapour must be at least five times as large as in the liquid, that curve E is proceeding towards higher pressures, starting from i .

In order to define the direction of curve E we define the values of λ_1 and λ_2 according (9) from:

$$1 + \lambda_1 + \lambda_2 = 0 \quad \text{and} \quad \lambda_1 x_1 + \lambda_2 x_2 = 0$$

(11) then passes into:

$$\left(\frac{dP}{dT}\right)_x = \frac{x_2(H_1 - H) - x_1(H_2 - H)}{x_2(V_1 - V) - x_1(V_2 - V)} \quad \dots \quad (38)$$

by which the direction of curve E is defined. This direction, as follows from (37), is dependent on the partition ($x_2 : x_1$) of the new substance between gas and liquid. Also it follows from (37) that curve E must be situated between the curves (L) and (G).

We now add a new substance which forms mixed-crystals with F , but which does not occur in the vapour. When we represent its concentration in F and L by x and x_1 then it follows from (29) and (32):

$$\Sigma(\lambda x)_V = \lambda_1 x_1 - x \quad \text{and} \quad \Sigma(\lambda x)_H = x - \mu_1 x_1$$

consequently:

$$(dT)_x = \frac{RT(x - \lambda_1 x_1)}{\Sigma(\lambda H)_V} \quad \text{and} \quad (dP)_x = \frac{RT(x - \mu_1 x_1)}{\Sigma(\lambda V)_H} \quad \dots \quad (39)$$

It is apparent from (30) and (33) that $\lambda_1 < 1$ and $\mu_1 > 1$, but also that λ_1 differs very little only from 1. It follows from (39):

$$\text{for } \frac{x}{x_1} > \mu_1 \quad \text{is} \quad (dT)_x > 0 \quad \text{and} \quad (dP)_x > 0;$$

Curve E is situated then, f.i. like curve id in fig. 1

$$\text{for } \mu_1 > \frac{x}{x_1} > \lambda_1 \quad \text{is} \quad (dT)_x > 0 \quad \text{and} \quad (dP)_x < 0;$$

Curve E is then situated, f.i. like curve ie in fig. 1

$$\text{for } \frac{x}{x_1} < \lambda_1 \quad \text{is} \quad (dT)_x < 0 \quad \text{and} \quad (dP)_x < 0;$$

Curve E then is situated f.i. as curve if in fig. 1.

In order to define the direction of curve E we take in accordance with (9):

$$\Sigma(\lambda) = 1 + \lambda_1 + \lambda_2 = 0 \quad \text{and} \quad \Sigma(\lambda x) = x + \lambda_1 x_1 = 0.$$

With the values of λ_1 and λ_2 which follow from this we find for (11):

$$\left(\frac{dP}{dT}\right)_x = \frac{x_1(H_2 - H) - x(H_2 - H_1)}{x_1(V_2 - V) - x(V_2 - V_1)} \quad \dots \quad (40)$$

so that the direction of curve E is defined.

Also it is apparent from (39) that E must be situated between the curves (F') and (L).

Finally we shall assume that the new substance divides itself over the three phases, we call its concentration in F L and G x_1 and x_2 . We now have according to (29) and (32):

$\Sigma (\lambda x)_I = -x + \lambda_1 x_1 + \lambda_2 x_2$ and $\Sigma (\lambda x)_{II} = x - \mu_1 x_1 + \mu_2 x_2$,
wherein $\lambda_1 + \lambda_2 = 1$ and $\mu_1 = 1 + \mu_2$, so that $(dT)_x$ and $(dP)_x$ are known.

We now put:

$$\Sigma (\lambda x)_I = r \text{ and } \Sigma (\lambda x)_{II} = s \quad . \quad . \quad . \quad (41)$$

As we are able to satisfy (40), independent on the values of r and s , by positive values of x x_1 and x_2 , it follows that curve E may go in every direction starting from point i . It may be situated, therefore, not only in one of the regions F and G , but also, like f. i. curve ig , in the region L . Of course its situation is dependent on the partition of the new substance between the three phases.

The same considerations as for fig 1 are also valid for fig 2, for this we have to examine however more in detail the occurrence of curve ic .

Instead of (25) we have for fig 2:

$$H_2 > H_1 > H \text{ and } V_2 > V_1 > V \quad . \quad . \quad . \quad (42)$$

As λ_2 is negative now, in accordance with (30) the isovolumetrical reaction passes into:



wherein:

$$\lambda_1 = \frac{V_2 - V}{V_2 - V_1} \text{ and } \lambda_2 = \frac{V_1 - V}{V_2 - V_1}$$

so that

$$\Sigma (\lambda H) = \lambda_1 H_1 - H - \lambda_2 G$$

is generally positive; reaction (43) is proceeding therefore, on addition of heat from left to right.

When we now add a new substance, which occurs in liquid and vapour, then we have: $\Sigma (\lambda x)_I = \lambda_1 x_1 - \lambda_2 x_2$. In order that $(dT)_x$ is positive, $\Sigma (\lambda x)_I$ must be negative, consequently:

$$\frac{x_2}{x_1} > \frac{\lambda_1}{\lambda_2} \text{ or } \frac{x_2}{x_1} > \frac{V_2 - V}{V_1 - V} \quad . \quad . \quad . \quad (44)$$

As in general $V_2 - V$ is some thousand times larger than $V_1 - V$ curve ic therefore can, occur only in the very special case that the concentration of the new substance is some thousand times larger in the vapour than in the liquid.

We may summarize some of the previous deductions in the following way.

When we add a new substance to an invariant unary equilibrium $E(x=0) = F + L + G$, then an equilibrium $E = F + L + G$ arises that is represented in the P, T -diagram by a curve E ; this curve begins in the invariant point i of the equilibrium $E(x=0)$.

When the new substance occurs in the liquid only, then curve E coincides with curve $(L) = F + G$ of the system $E(x=0)$.

When the new substance is occurring in liquid and vapour then curve E is situated in the region F ; its direction is defined by the partition of the new substance between vapour and liquid. A curve, like ic in fig. 2 may, however, occur only in very special circumstances.

When the new substance is occurring in liquid and solid phase (consequently with formation of mixed crystals) then curve E is situated in the region G ; its direction is defined by the partition of the new substance between mixed crystals and liquid.

When the new substance occurs in the three phases, then curve E may be situated in each of the three regions; its direction is defined by the partition of the new substance between the three phases.

(To be continued).

Leiden, Lab. of Inorganic Chemistry.

Mathematics. — *“Ueber Determinanten aus Formenkoeffizienten”.*

By B. L. VAN DER WAERDEN. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of October 28, 1922).

§ 1. Die Aufgabe.

Vier binäre Bilinearformen $(ax)(a'x')$ bestimmen die Determinante

$$\Delta = \begin{vmatrix} 1_{1,1} & 1_{1,2} & 1_{2,1} & 1_{2,2} \\ \vdots & & & \\ 4_{1,1} & & & \end{vmatrix}$$

(wo $1_{i,k}$ die Koeffizienten der ersten Form sind, usw.), welche invariant ist gegenüber unabhängigen linearen Transformationen der beiden binären Gebiete x und x' , weil bei diesen Transformationen auch die Koeffizientenreihen linear transformiert werden.

Sechs lineare Komplexe im dreidimensionalen Raum R haben ebenso eine Invariante

$$\Delta = \begin{vmatrix} 1_{12} & 1_{13} & 1_{14} & 1_{34} & 1_{42} & 1_{23} \\ \vdots & & & & & \\ 6_{12} & & & & & \end{vmatrix}.$$

Für das Problem: Derartige Invarianten symbolisch darzustellen, werde ich im Folgenden eine allgemeine Methode angeben und diese dann auf die genannten zwei Beispiele anwenden.

§ 2. Lemma.

Wenn eine Form f in n n -ären Veränderlichen (eine n -äre Veränderliche ist ein Inbegriff von n homogenen Grössen $x_1 \dots x_n$), sich gegenüber Permutation dieser Veränderlichen verhält wie eine alternierende Funktion, so enthält sie entweder den Klammerfaktor $(xy \dots)$, oder sie verschwindet identisch.

Beweis. Setzt man zwei der Veränderlichen einander gleich, so verschwindet f identisch, da dann $f = -f$ wird. Wenn man dann nach dem Gleichsetzen mit Polarenprozessen operiert, so erhält man immer wieder identisch Null. Also verschwindet das erste Glied der GORDAN-CAPELLI-schen Reihenentwicklung der Form f identisch. Alle weiteren Glieder aber enthalten entweder den Faktor $(xy \dots)$, oder verschwinden. Daraus folgt das Lemma.

Bemerkung. Für den Fall (den ich eben benötige), wo die x, y, \dots in f linear auftreten, ist das Lemma elementarer zu beweisen. Es ist dann nämlich symbolisch

$$f = A \cdot (a' x) (b' y) \dots$$

Vertauscht man x, y, \dots in allen möglichen Weisen, und addiert mit \pm , so kommt

$$n! f = A \begin{vmatrix} (a' x) (a' y) \dots \\ (b' x) (b' y) \dots \\ \vdots \\ \vdots \end{vmatrix},$$

oder nach dem Multiplikationssatze der Determinanten

$$n! f = A \cdot (a' b' \dots) (x y \dots)$$

$$f = \frac{A}{n!} (a' b' \dots) (x y \dots).$$

§ 3. Die allgemeine Methode.

Es seien gegeben N Formen derselben Art, mit je N Koeffizienten. Ich setze voraus, dass man alle Invarianten vom 1. Grade in den Koeffizienten dieser Formen, symbolisch hingeschrieben hat. Verlangt wird dann, die Determinante Δ der N^2 Koeffizienten durch diese Invarianten auszudrücken. Lösung: Man stelle aus diesen Invarianten irgendeine alternierende Funktion der Koeffizientenreihen her. Wenn diese nicht identisch verschwindet, so stellt sie nach dem Lemma bis auf einen konstanten Faktor die gesuchte Determinante Δ dar.

In manchen Fällen gelingt das Auffinden einer solchen alternierenden Funktion sogleich. Ist dies nicht der Fall, so kann man so verfahren: Man wähle irgendeine lineare Invariante I des Systems, und bilde

$$\Sigma \pm I$$

unter Vertauschung der Formen in allen möglichen Weisen. Es gibt wegen der Existenz von Δ sicher mindestens eine Invariante I , für welche diese Bildung nicht identisch verschwindet, und die Bildung stellt dann nach § 2, weil sie alterniert, bis auf einen konstanten Faktor die gesuchte Invariante Δ dar.

§ 4. Erstes Beispiel. Vier Bilinearformen in zwei unabhängigen binären Veränderlichen.

Die Invarianten der Formen $(1x)(1'x'), \dots, (4x)(4'x')$ gehören den

folgenden Typen an: ¹⁾

$$\begin{cases} B_{12} = (12) (1' 2') = B_{21} \\ F_{1234} = (12) (2' 3') (34) (4' 1') = F_{3412} = F_{4321} = F_{2143} \end{cases}$$

Die Invarianten vom 1. Grade in den Koeffizienten der 4 Formen sind also:

$$\begin{cases} B_{12} B_{34}, B_{13} B_{24}, \text{ usw.} \\ F_{1234} \quad \quad \quad , \text{ usw.} \end{cases}$$

Nun ist

$$\Sigma \pm B_{12} B_{34} \equiv 0$$

es bleibt also für Δ nur die Möglichkeit:

$$\begin{aligned} \Delta &= A \cdot \Sigma \pm F_{1234} \\ &= 4A \cdot \{ F_{1234} - F_{1234} - F_{1324} + F_{1423} + F_{1342} - F_{1432} \}. \end{aligned}$$

Zur Bestimmung der Konstanten A genügt das Zahlenbeispiel

$$\Delta = \begin{vmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & & \\ & & \cdot & \\ & & & \cdot \end{vmatrix}.$$

Das gibt

$$A = -\frac{1}{12}.$$

Um nun $\Sigma \pm F_{1234}$ in seiner einfachsten Form darzustellen, verwenden wir die sich aus

$$(2' 3') (4' 1') = (2' 4') (3' 1') + (1' 2') (3' 4')$$

ergebende Identität

$$F_{1234} = -F_{1243} + B_{12} B_{34}$$

Diese erlaubt uns, zwei beliebige F_{ikln} aufeinander zu reduzieren (durch wiederholtes Vertauschen von aufeinanderfolgenden Indizes). So reduzieren wir die letzten fünf Glieder der angeschriebenen Entwicklung für Δ auf das erste. Es kommt schliesslich

$$\Delta = -2F_{1234} + B_{12} B_{34} - B_{13} B_{24} + B_{14} B_{23}.$$

Wenn man will, kann man auch schreiben

$$\Delta = -F_{1234} + F_{2341}.$$

§ 5. Zweites Beispiel. Sechs lineare Komplexe im Quaternären.

Geschrieben in WEITZENBÖCK—WAELSCH'schen Komplexsymbolen²⁾, sind alle Invarianten von linearen Komplexen reduzibel auf „Ketten“, wie

¹⁾ Da die beiden binären Gebiete unabhängig transformiert werden, so bestehen die Invarianten aus Klammerfaktoren, deren Symbole beide demselben Gebiete angehören.

²⁾ Siehe R. WEITZENBÖCK, Komplex-Symbolik, Leipzig 1908, WAELSCH, Wiener Berichte Dec. 1889, oder besser den III. Abschnitt der in Kurzem bei Noordhoff Groningen erscheinenden „Invariantentheorie“ von R. WEITZENBÖCK.

$$[12'] = (1'2)(21') = (1'2)^2 = [21'] \dots \dots \dots (1)$$

$$\begin{aligned} [12'34'56'] &= (12')(2'3)(34')(4'5)(56')(6'1) = [34'56'12'] = \\ &= [56'12'34'] = [16'54'32'] = \text{etc.} \end{aligned} \quad (2)$$

Die Viererkette ist reduzibel¹⁾, vermöge²⁾

$$[12'34'] = \frac{1}{2} \{ [12'] [34'] - [13'] [24'] + [14'] [23'] \} \dots (3)$$

Zwei Sechserketten die auseinander entstehen durch Vertauschen zweier aufeinanderfolgender Indizes, sind zueinander reduzibel vermöge der Identität³⁾

$$(xp')(p'q)(q'u') + (xq')(q'p)(p'u') = -\frac{1}{2} [pq'](u'y),$$

zufolge welcher

$$[12'34'..] + [13'24'..] = -\frac{1}{2} [23'] [14'..] \dots (4)$$

und dual dazu. Aus (3) und (4) folgt noch

$$\begin{aligned} [12'34'56'] &= -[13'24'56'] - \frac{1}{8} \{ [23'] \{ [14'] [56'] - [15'] [46'] + [16'] [45'] \} \} \\ \text{und dual dazu} & \\ [12'34'56'] &= -[21'34'56'] - \frac{1}{8} \{ [12'] \{ [34'] [56'] - [35'] [46'] + [36'] [45'] \} \} \end{aligned} \quad (5)$$

Um nun die Invariante

$$\Delta = \begin{vmatrix} 1_{12} & 1_{13} & 1_{14} & 1_{34} & 1_{42} & 1_{23} \\ \vdots & & & & & \\ 6_{12} & & & & & \end{vmatrix} .$$

symbolisch darzustellen, bemerken wir, dass

$$\Sigma \pm [12'] [34'] [56'] \equiv 0.$$

Also bleibt als einzige Möglichkeit

$$\Delta = A \cdot \Sigma \pm [12'34'56'].$$

Zur Bestimmung von A nehmen wir das Zahlenbeispiel

$$\Delta = \begin{vmatrix} 1 & 0 & \dots \\ 0 & 1 & \\ \vdots & & \end{vmatrix}$$

und erhalten

$$A = -\frac{2}{8},$$

also

$$\Delta = -\frac{2}{6!} \Sigma \pm [12'34'56'] \dots \dots \dots (6)$$

Man könnte nun, so wie im vorigen §, diesen Ausdruck weiter

¹⁾ Die Sechserkette ist nicht reduzibel. Vergl. R. WEITZENBÖCK, Jahresber. D. Math.-Ver. 19 (1910) und Wiener Ber. 122 (1913).

²⁾ R. WEITZENBÖCK, Invariantentheorie III, § 5 Gl. (10).

³⁾ Komplex-Symb. p. 8, (26) und (26a); Invariantentheorie III, § 5 Gl. (4).

reduzieren mittels (5); dann aber hätte man 119 Glieder zu berechnen, und an jedem Gliede eine bis zehn Reduktionen vorzunehmen. Man weiss aber im Voraus, dass das Resultat die Form

$$\Delta = -2 [12'34'56'] + F' \{ [12'], \dots, [56'] \} \quad . \quad . \quad . \quad (7)$$

haben muss. Wenn diese Formel gilt, so muss die duale auch gelten. Um Δ zu dualisieren, muss man $1_{1,}$ durch $1'_{1,}$, oder durch $1_{1,}$ ersetzen, usw.: Δ geht dann über $-\Delta$. Jede Zweierkette ist zu sich selbst dual. Also kommt

$$-\Delta = -2 [1'23'45'6] + F' \{ [12'], \dots, [56'] \} \quad . \quad . \quad . \quad (8)$$

Subtrahiert man nun (7) und (8), so fällt die Funktion F' heraus, und man erhält Δ in der Form:

$$\Delta = - [12'34'56'] + [1'23'45'6] \quad . \quad . \quad . \quad . \quad (9)$$

Wenn man will, kann man für $[1'23'45'6]$ auch schreiben $[61'23'45']$, und das zweite Glied durch wiederholte Anwendung von (5) auf das erste reduzieren; es kommt schliesslich

$$\begin{aligned} \Delta = & -2 [12'34'56'] - \frac{1}{8} \{ [12'] [34'] [56'] + [23'] [45'] [61'] \} \\ & + \frac{1}{8} \{ [12'] [35'] [46'] + \text{cykl} \} \\ & - \frac{1}{8} \{ [14'] [23'] [56'] + ck \} \\ & - \frac{1}{8} \{ [14'] [26'] [35'] + ck \} \\ & + \frac{1}{8} [14'] [25'] [36'] \end{aligned} \quad \left. \vphantom{\Delta} \right\} (10)$$

wo $[..][..][..] + \text{cykl}$. bedeutet: die Summe aller Glieder, die aus dem angeschriebenen Gliede entstehen durch null- bis fünf-malige

Anwendung der Permutation $\begin{Bmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ 2 & 3 & 4 & 5 & 6 & 1 \end{Bmatrix}$, während $[..][..][..] + ck$

bedeutet: die Summe aller Glieder, die aus dem angeschriebenen entstehen durch null- bis zwei-malige Anwendung der Permutation

$$\begin{Bmatrix} 12 & 34 & 56 \\ 34 & 56 & 12 \end{Bmatrix}.$$

Chemistry. — “*The dissociation constants of sulphonacetic and α -sulphonpropionic acids*”. By Prof. H. J. BACKER. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated at the meeting of September 30, 1922).

The α -sulphoncarboxylic acids are dibasic acids with a strong and a weak acid function.

Consequently, the free compounds belong to the strong acids, whilst the acid salts behave as weak acids.

In the table the molecular conductivity of sulphonacetic and α -sulphonpropionic acid is mentioned.

When the values at an infinite dilution μ_{∞} , on account of the number of atoms in a molecule¹⁾ are taken for the sulphonacetic acid at 376, and for the sulphonpropionic acid at 373, then the mean value of the dissociation constant, at the concentrations $1/32$ and $1/64$ Grammolecule per litre, is found to be for the sulphonacetic acid 0.58 and for the sulphonpropionic acid 0.57.

Great accuracy can not be ascribed to these figures, as the uncertainty in the determination of μ_{∞} in the case of these strong acids has a great influence on the size of the constants.

However, the values are not improbable; for WEGSCHEIDER²⁾, who has argued the validity of OSTWALD'S dilution law for sulphonic acids, has calculated for benzol sulphonic, p-toluolsulphonic and β -naphthalinesulphonic acids, the constants 0.21, 0.214 and 0.267, and for the m-sulphonbenzoic acid, related to the above-mentioned acids, the constant 0.4.

In the solutions of the acid sodium salts of the sulphoncarboxylic acids chiefly the following ionic equilibria exist:



Besides, molecules of the free acid may be formed:



The conductivity of the acid sodium salts is thus caused by the ions: Na', HA', H', A''.

¹⁾ OSTWALD-LUTHER, Hand- u. Hilfsbuch 1922, 482.

²⁾ WEGSCHEIDER, Monatshefte f. Ch. 23, 340, 341 (1902); 30, 440 (1909).

Molecular conductivity at 25° C. in reciprocal Ohms¹⁾.

| V (Number of liters p. G. mol.) | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|-------|-------|-------|-------|-------|-------|-------|
| Sulphonacetic acid $C_2H_4O_5S$ | 348.9 | 357.9 | 366.3 | 373.3 | 380.1 | 388.8 | 403.4 |
| Monosodium sulphonacetate $C_2H_3O_5SNa$ | 88.4 | 98.4 | 110.1 | 123.9 | 141.0 | 163.2 | 191.4 |
| Disodium sulphonacetate $C_2H_2O_5SNa_2$ | 162.5 | 180.0 | 194.0 | 206.0 | 215.2 | 223.0 | 228.8 |
| Sulphonpropionic acid $C_3H_6O_5S$ | 345.5 | 355.5 | 362.8 | 369.0 | 373.3 | 379.4 | 387.4 |
| Monosodium sulphonpropionate $C_3H_5O_5SNa$ | 82.6 | 91.4 | 101.1 | 112.5 | 126.3 | 146.0 | 169.0 |
| Disodium sulphonpropionate $C_3H_4O_5SNa_2$ | 154.8 | 169.3 | 182.0 | 192.6 | 201.0 | 208.0 | 213.2 |
| Propionanilide- α -sulphonic acid $C_9H_{11}O_4SN$ | 337.2 | 348.1 | 355.7 | 360.8 | 364.0 | 365.1 | 365.2 |
| Sodium propionanilide- α -sulphonate $C_9H_{10}O_4SNNa$ | 63.0 | 66.6 | 69.6 | 71.4 | 73.3 | 74.9 | 76.3 |

In order to get an idea of the dissociation constant k_2 of reaction II, the conductivity of the acid salts must be diminished by the contributions of the ions Na^+ and HA' .

The conductivity of the HA -ions $\lambda_{HA'}$ may, on account of the number of atoms, be estimated for the sulphonacetic acid at 36 and for the sulphonpropionic acid at 33.

Further, the dissociation degree α_1 of reaction I has to be known.

This value being not directly determinable, we may make use of BREDIG's rule²⁾, that the dissociation degree of the sodium salts of different monobasic acids rises about equally rapidly on diluting the solution.

It is therefore allowable to take the dissociation degrees sought

¹⁾ Only the conductivities of the neutral salts have been diminished by the conductivity of the water ($1.5-2.0 \times 10^{-6}$).

²⁾ BREDIG, Z. f. phys. Ch. 13, 191 (1894).

as equal to the values given by the sodium salt of an analogically built acid in the same dilution. As the properties of the acid salts of the α -sulphonic acids indicate the structure $\text{CHR}(\text{CO}_2\text{H})\text{SO}_3\text{Na}$, the sodium salt of a sulphonic acid may be chosen for the sake of comparison.

Now, with a view to determine the dissociation degree of a monobasic sulphonic acid, related to the acids in question, the anilide of sulphonpropionic acid was prepared ¹⁾. The conductivity mentioned in the table shows that this propionanilide- α -sulphonic acid is a strong acid, from which it follows with certainty, that the sulphonic acid group is free and that the carboxylic group is changed into amide: $\text{CH}_3 \cdot \text{CH}(\text{CONHC}_6\text{H}_5) \cdot \text{SO}_3\text{H}$.

If μ_∞ is assumed to be 368, a value resulting from the conductivity of the sodium salts and also from the number of atoms, then the mean dissociation constant for the dilutions 64, 128 and 256 is found to be 0,39.

For the sodium salt, the conductivities at the dilutions 256, 512 and 1024, extrapolated according to BREDIG, give $\mu_\infty = 79,0$.

From this results the ionisation degree α at the dilutions v :

| | | | | | | | |
|------------|-------|-------|-------|-------|-------|-------|-------|
| $v =$ | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
| $\alpha =$ | 0,797 | 0,843 | 0,881 | 0,904 | 0,928 | 0,948 | 0,966 |

These values are also taken for α_1 , the dissociation degree of NaHA (réaction I).

The conductivity of the acid salt μ_{NaHA} , diminished by $\alpha_1(\lambda_{\text{Na}^+} + \lambda_{\text{HA}'})$, will give, as a first approximation, the conductivity due to the ions H^+ and A'' .

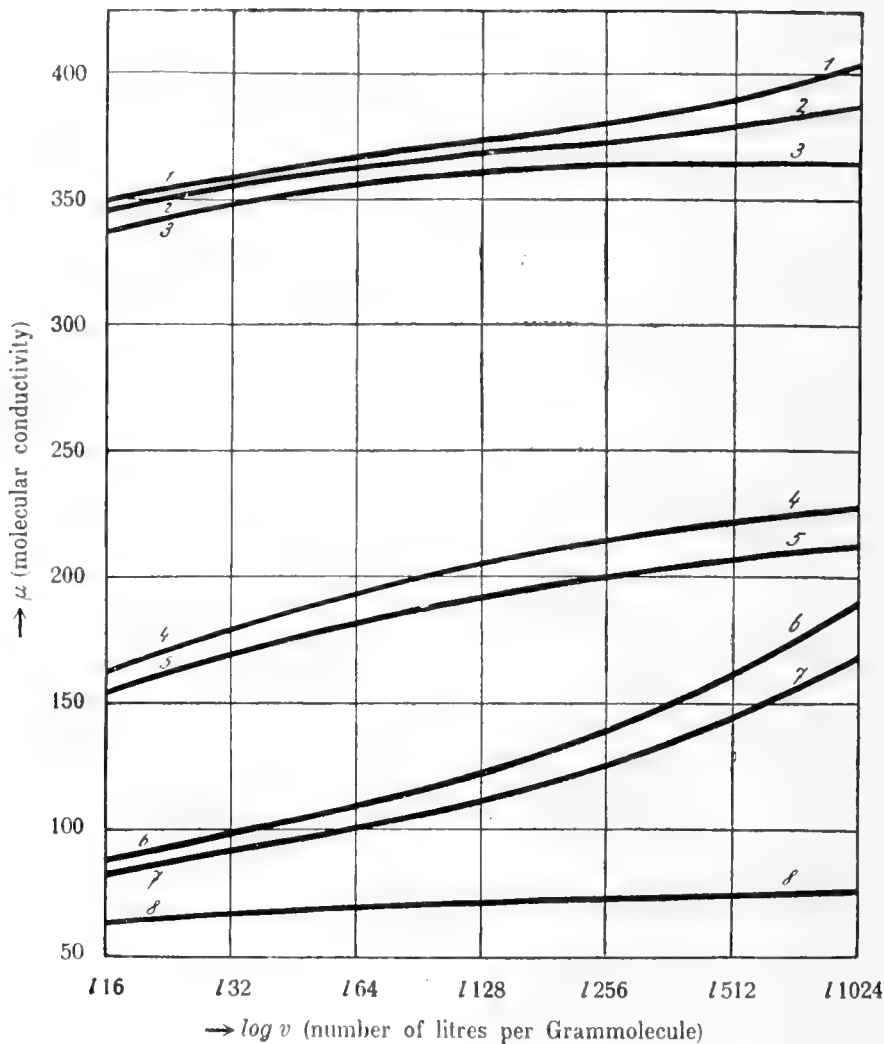
In order to get a value for k_2 , it is necessary to know the conductivity which the ions H^+ and A'' would give at a complete ionisation according to reaction II.

The equivalent conductivity of the neutral sodium salts diminished by λ_{Na^+} , gives $\lambda_{\text{A}''}$. In this way the value 72 was found for sulphonacetic acid and 65 for sulphonpropionic acid.

The conductivity of the ions H^+ and A'' at infinite dilution is then expressed by $\lambda_{\text{H}^+} + 2\lambda_{\text{A}''}$.

The observed conductivity $\mu_{\text{NaHA}} - \alpha_1(\lambda_{\text{Na}^+} + \lambda_{\text{HA}'})$, divided by this value $\lambda_{\text{H}^+} + 2\lambda_{\text{A}''}$, gives, as a first approximation, the value of α_1 , the dissociation degree of reaction II.

¹⁾ Recueil d. tr. ch. 40, 585 (1921).



Molecular conductivity.

1. Sulphonacetic acid.
2. Sulphonpropionic acid.
3. Propionanilide- α -sulphonic acid.
4. Disodium sulphonacetate.
5. Disodium sulphonpropionate.
6. Monosodium sulphonacetate.
7. Monosodium sulphonpropionate.
8. Sodium propionanilide- α -sulphonate.

Now, a correction may be made for the fact that the concentration of the HA'-ions is smaller than agrees with reaction I,

these ions being further split up according to reaction II.

A corrected value for α_2 is obtained, from which k_2 may be calculated.

In this way k_2 is found to be for the sulphonacetic acid:

$$\begin{array}{r} v = 16 \quad 32 \quad 64 \quad 128 \quad 256 \quad 512 \quad 1024 \\ k_2 = 11.3 \quad 10.1 \quad 9.2 \quad 8.6 \quad 8.0 \quad 7.6 \quad 7.3 \times 10^{-5} \end{array}$$

and for the sulphonpropionic acid:

$$\begin{array}{r} v = 16 \quad 32 \quad 64 \quad 128 \quad 256 \quad 512 \quad 1024 \\ k_2 = 7.8 \quad 7.0 \quad 6.3 \quad 5.8 \quad 5.3 \quad 5.2 \quad 4.8 \times 10^{-5} \end{array}$$

The mean value of the second dissociation constant thus becomes for the sulphonacetic acid 8.9×10^{-5} and for the sulphonpropionic acid 6.0×10^{-5} .

In this statement of views no account is taken of the combination of the ions H^+ and HA' , as shown by reaction III.

A correction for this last, however, that would somewhat increase the second dissociation constant is of no value for these strongly dissociated acids, as the uncertainty in the values of the conductivity of the different ions has a greater influence.

Dr. O. RINGER and Drs. D. W. DIJKSTRA have given their assistance with some of the measurements.

A more detailed account will appear in the *Recueil d. trav. chim.*

Organic Chemical Laboratory of the University.

Groningen, 8th Sept. 1922.

Physiology. — “*On the progress of the veratrin-poisoning of the striated frog-muscle*”. By ARIE QUERIDO. (Communicated by Prof. G. VAN RIJNBERK).

(Communicated at the meeting of October 28, 1922.)

1. *Concentration and dose.*

The nature of the action of veratrin on the striated muscular tissue still has not been sufficiently revealed, partly because of the lack of knowledge of the conditions, associating the poisoning. Repeatedly we read with various authors the remark, how fickle and incalculable the veratrin-phenomenon is in its appearance, seemingly independent of the quantity of poison used and the time it could act. It is true in 1904 MOSTINSKY¹⁾ examined the factors cooperating in the formation of a definite shape of curve and he succeeded in ascertaining the conditions incidental to this; the modifications however of these conditions in the course of an experiment, i. e. the alterations during the poisoning of the balance between muscle-metabolism and poison-action of which the curve is a result, are unknown as yet. Closely connected with this is the question, in what way the shape of the curve corresponds with the rate of poisoning of the muscle. On this subject we have some information, that is two types of contraction-shape are distinguished, viz. the type with two and with one top (fusion type), the latter of which corresponds to a stronger rate of poisoning (BOEHM²⁾, DEELMAN³⁾).

In order to study these questions further, I irritated muscle-nerve-preparations, after their immersion in a veratrin-Ringer-solution, by induction-shocks with so long a pause between the stimulations, that the influence of a contraction on the following need not be taken into account (three minutes).

In this way I collected a great number of curves of veratrin-poisonings for different concentrations of the poison. On contemplating the modifications in the veratrinogram, we can get an idea of the relation between curve and rate of poisoning, for if a poisoning is seen to progress in the direction of a diminishing or vanishing

1) Arch. f. exp. Path. u. Pharm., 51, 1904,

2) Idem 71, 1913.

3) Contrib. to Biology from the Amsterdam University 1914—15.

poison-influence, proved by the final appearance of normal, single, rapid contractions, we see, before this stage is reached, the second shortening becoming lower, of a shorter duration and appearing after a longer latent period; conversely it follows that a strong poisoning will be expressed by a high, prolonged, second shortening, having a short latent period and that the "fusion type" indeed corresponds with a stronger rate of poisoning than one with two tops, for with the former the latent period has reached its minimum, i.e. has grown equal to that of the first shortening; moreover the height is greater than that of a non-fusion second top. These magnitudes therefore, which may be expressed in the corresponding magnitudes of the first contraction, give a relative standard, holding for each separate muscle during the course of an experiment, for the poisoning at the moment of contraction, enabling us to picture to ourselves the progress of the poisoning, without our being dependent on the direct result, viz. the shape of the curve.

On studying the poisoning-process in this way, we notice in the series of curves peculiar differences, dependent on the concentrations, in which the poison has been applied.

1. In concentrations of 1:1000 and higher the muscle contracts as soon as it is brought into touch with the solution and maintains that shortening. On being stimulated the muscle shows either a very

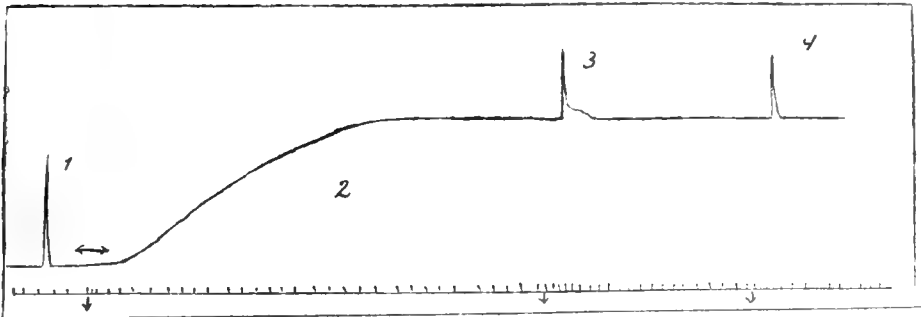


Fig. 1.

Experimental-process, when a veratrin-Ringer solution 1:1000 is poured on a muscle-nerve-preparation.

1: Contraction before poisoning: Af \longleftrightarrow : pouring on the solution. 2: subsequent contraction of the muscle; 3 and 4: contraction after electric stimulation, three, resp. six minutes after application of the solution: at \downarrow the cylinder stopped. Time $\frac{1}{6}$ sec.

slight veratrin-effect, or there is no result at all of the veratrin-poisoning, and the concentration is undistinguishable from the contraction yielded by an unpoisoned muscle on single stimulation.

(Fig. 1). This reaction is soon succeeded by complete insensibility for stimulation.

2. If the muscle has been put into a veratrin-solution weaker than 1:1000, but stronger than 1:100000 a series of curves is obtained, of which either the first or a following gives the strongest picture of the typical veratrin-poisoning, after which this effect diminishes till it finally disappears, so that the muscle, just as before the poisoning, responds to the stimulation with a single, rapid contraction, if at least it has not become insensitive, before this stage has been reached.

3. If solutions of 1:100000 and weaker are employed, a definite effect of the veratrin-action is obtained, which can maintain itself for hours together when the preparation is regularly stimulated.

There are three hypotheses which might explain the process described sub 1 and 2.

A. When the muscle has absorbed a certain quantity of poison and gradually diminishes the effect of this by its contractions — no matter how this happens — it is no more able to stand the influence of veratrin again.

B. The quantity of poison in the solution is not sufficient to supply the quantity abolished by the muscle.

C. In the period between two contractions the muscle modifies its character in such a way, that it grows less sensitive to veratrin-influence.

Hypothesis *A* may be omitted: a muscle once poisoned by veratrin can very well be influenced by veratrin-action again, after the veratrin-effect has been abolished by repeated contracting (e.g. by frequent stimulation), as the experiment teaches.

Hypothesis *B* may also be omitted, because VON FREY's¹⁾ experiments show, that minimum quantities are already sufficient to poison a muscle. Therefore the hypothesis remains, that the muscle alters its character in the period of time between two stimulations, a modification which can only be attributed to the action of veratrin, for if all circumstances are left unchanged and only the veratrin-concentration is altered, a definite rate of poisoning occurs, which appears to be constant (third process).

Evidently there exists, besides the veratrin-effect on the striated muscle, causing the well-known second shortening, another action, having an unfavourable influence on the effect first-mentioned, and causing a rapid and exhaustive effect in strong concentrations, in

¹⁾ Sitzungsber. der Physik.-Med. Gesellsch., Würzburg, 1912.

less strong ones a slow and gradual effect; while below a certain concentration it can no more occur.

If the poisoning-process in a calf-muscle, which is left in situ is studied here — again with a stimulation-interval of three minutes — the process mentioned sub 1 is never observed, because the veratrin-concentration in the blood never reaches a sufficient height. On employing large doses (e. g. 15 mgr. per 50 Gr. frog) the heart is arrested after a short time as BOEHM¹⁾ describes it and the muscle is in no other relation — not considering a more intensive contact with the veratrin-solution — than in a muscle-trough of KEITH LUCAS, filled with a solution of the concentration at which the process mentioned sub 2 occurs; the conduct of the muscle is indeed in absolute accordance with this. On using smaller doses (1—2 mgr. per 50 Gr. frog), the heart, at least during the first hours after poisoning, keeps beating, only gradually diminishing its frequency; consequently the quantity of veratrin carried to the muscle is steadily increased and it should be borne in mind, that when the veratrin-concentration exceeds a definite threshold, the second effect of veratrin mentioned above will make its influence felt, i. o. w. the poisoning will seem less intensive: conversely every contraction will abolish part of the veratrin-effect and it may be supposed that in this way interference takes place between the influence of the two factors, determining the effect of the rate of poisoning, viz. the application and the rendering inactive of veratrin, when their two causes, i. e. the heart-action and the lapse of time between two contractions, occur in a definite proportion. As a result of this interference a periodicity occurs in the poisoning-process, i. e. the effects of stronger poisoning (higher, more prolonged second top) vary with those of less strong poisoning. At length the regularity of these oscillations is interrupted, because the heart-action diminishes under influence of the effect of the poison and the relation above-mentioned exists no more.

A constant poisoning in a muscle in situ can only then be obtained when the poison is applied without interference of the heart, e. g. by subcutaneous muscular injection (BUCHANAN²⁾).

2. *Combination of veratrin and curare.*

DE BOER³⁾ communicates the possibility of leaving only the second shortening by simultaneous application of veratrin and curare. He

¹⁾ Arch. f. exp. Path. u. Pharm., 71, 1913.

²⁾ Journ. of Physiol. 1899.

³⁾ Contributions Amsterdam 1914—15 and Zeitschr. f. Biol. 65.

gives few particulars however, so that I did not think it superfluous to repeat this experiment. It appears that quite different processes may arise, dependent on the lapse of time between the application of the two drugs.

A. If veratrin is first injected and the application of curare is put off till a distinct veratrinogram appears, the curare-injection remains without perceptible effect, the veratrin-poisoning proceeds as usual.

B. If curare is injected either simultaneously with veratrin-or so short a time after, that the veratrin-effect has not yet become manifest in the shape of a curve, in the further course of the experiment a typical veratrinogram appears, which shows that the two parts are equally effected by curare, so that both of them diminish till complete indirect insensibility; on direct stimulation the muscle even then gives a typical veratrinogram.

C. If veratrin is applied, if there is already an outspoken curare-poisoning, no veratrin-effect is shown, the poisoning behaves as a common curare-action till complete indirect insensibility.

D. If veratrin is injected while there are slight effects of the curare-action — it is of course impossible to mention objective data on this subject — in the further progress a veratrinogram appears with a usually very striking second top, which is afterwards modified into a normal-looking veratrinogram, which further behaves as such.

E. Finally veratrin may be injected between the stages *C* and *D*; then there arises neither a rapid contraction nor a veratrinogram, but a muscle-contraction, which should be identified the second shortening of the veratrin-curve. On direct stimulation there is also formed a typical veratrinogram in that case. (Fig. 2). The further process may lead to complete indirect insensibility, or to the fact that before this slow contraction there occurs a rapid one, causing another typical veratrinogram. In shape the shortening thus obtained is identical to the second contraction of a veratrinogram, when this succeeds the first in isolated condition, as it is sometimes seen during a poisoning-process.

Examined on a quick-turning cylinder its latent period appears to be twice or four times as long again as that of a normal single contraction; no top is formed, the highest part of the contraction is a horizontal line; the crescent is much less steep than the decrescent; the duration amounts to one to four seconds.

3. *Temperature.*

As to the influence of temperature, I agree in general with BRUNTON

and CASH¹⁾, according to whom both high and low temperatures have an unfavourable influence on the veratrin-phenomenon.

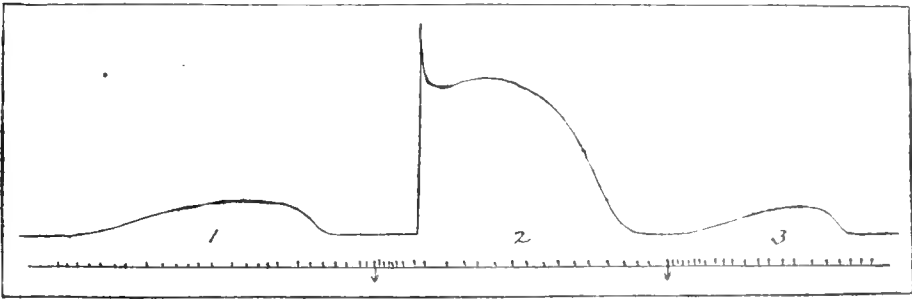


Fig. 2.

Combined action of veratrin and curare; 1 and 3: contraction on indirect stimulation; 2: contraction on direct stimulation; period between contractions: three minutes; at ↓ the cylinder stopped. Time $\frac{1}{6}$ sec.

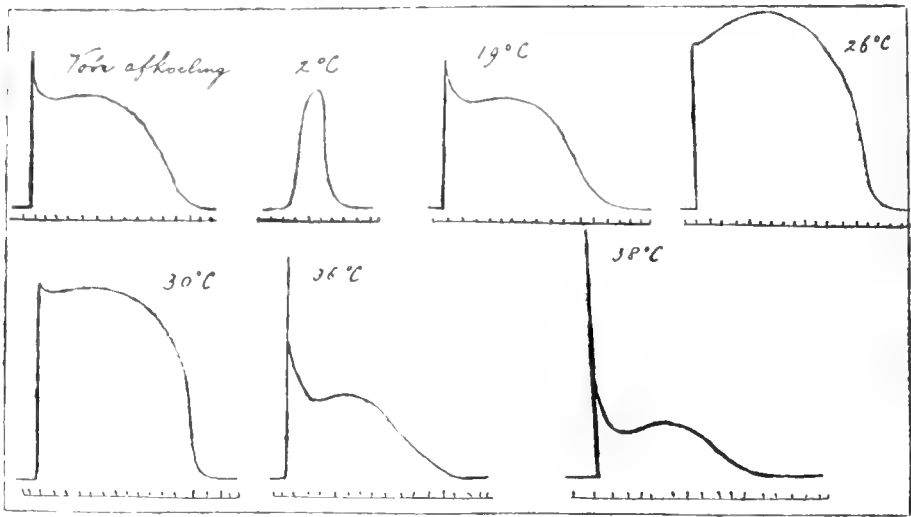
Here too a number of details are to be observed with respect to the modifications, the veratrinogram undergoes at various temperatures.

If a frog is cooled to 4° C. or lower and a veratrin-injection is given after that, no poisoning-effect is observed; the muscle behaves as an unpoisoned, cooled muscle, giving a relatively long and low contraction on induction-irritation. If the frog is subsequently heated, the second shortening gradually appears, first rapidly and of a short duration; above 14° C. the normal veratrinogram appears; conversely if a frog already poisoned is cooled, the second shortening disappears in quite the same way as it appears in the reverse experiment. Here too the cooled muscle behaves like an unpoisoned one. On heating above room-temperature the second shortening is seen to increase (in height as well as in duration). The first also increases its height as the contraction of an unpoisoned muscle would do, the second however increases more rapidly and consequently soon exceeds the first in size, so that a "fusion" type of curve arises.

At about 30 degrees the second shortening still increases in size, now however the first grows more rapidly and at $\pm 36^\circ$ the second shortening begins to decrease also absolutely, the first behaves exactly as the contraction of an unpoisoned muscle would do; till the muscle has become insensitive in consequence of heat-stiffness, there is still some veratrin-effect left. (Fig. 3). All this occurs quite independently of the poisoning-process; from every temperature with its corresponding

¹⁾ Journ. of Physiol. 1883.

curve-shape, we can return to room-temperature and see a typical veratrinogram arise.



Voor afkoeling = Before cooling.

Shapes of veratrinogram, yielded by one muscle at various temperatures. Time $\frac{1}{6}$ sec.

4. *Strength of stimulus.*

I have not succeeded in exercising an influence on one of the two parts of the veratrinogram separately by means of the strength of the stimulus. If the strength of the stimulus is gradually diminished, we may observe as MOSTINSKY¹⁾ describes, the critical progress of the excitability of the veratrin-muscle, i.e. below a definite limit, which is very exact, no reaction occurs on irritation, above this limit a reaction, differing but little from the maximal; moreover this always is a complete veratrinogram.

„A more detailed research concerning the problem of veratrin will appear in the „Archives de Physiologie Néerl.””

¹⁾ loc. cit.

Anatomy. — "*The Problem of Orthognathism*". By Prof. L. BOLK.

(Communicated at the meeting of October 28, 1922).

In the meeting of February 1921 I called attention to the fact that the typically somatic human features are of a special character, viz, they are persisting fetal properties and conditions. I referred this fact to the influence of the endocrin system, which, through its inhibitive action, fixes fetal morphogenetic relations. The character of the human body, therefore, is its fetality, and this character results from what I am inclined to term a process of fetalization.

When studying the structure of the human skull from this point of view, it is surprising to note how all at once the whole complex of the typically human features, — and there are many in the skull — becomes easy of comprehension. Of all parts of the human body the head is most indicative of its fetal character. Earlier researches made by me had already favoured this view with regard to several of these properties. Long before conception of the fetalization-principle as the leading factor in the genesis of the human body as a whole, I had already pointed out that many somatic property of man represents an early stage of ontogenetic development.

However, there was one property of the skull about which I had no fixed opinion, and it is just this property that determines so emphatically the human physiognomy viz. its orthognathism. The question urged itself upon me, whether also this feature should be a persisting fetal property? I felt some diffidence in putting the question, as the pronouncements laid down in the literature were not very encouraging, the general conception being that the orthognathous (i.e. the human) skull-type has originated from the prognathous (i.e. the animal) type. The evolution is supposed to have consisted in a shortening of the jaws, in connection with the presumed reduction of the set of teeth. Now, to this conception objections might be raised also from other quarters, but I deemed it necessary, instead of opposing one speculation to another, to let the facts speak for themselves. This led me to an inquiry into the relation between prognathism and orthognathism. The results were indeed surprising, for not only was I in a position to establish this relation, but it also became evident that the whole complex of

human properties in the skull form one entity. However, in this paper I shall confine myself to my real subject.

My first attempt was to ascertain the essential morphological features of the prognathous and the orthognathous skull-type, for the criterion of short or long jaws is inadequate. With the aid of Figs 1 and 2 these features are easy to establish.

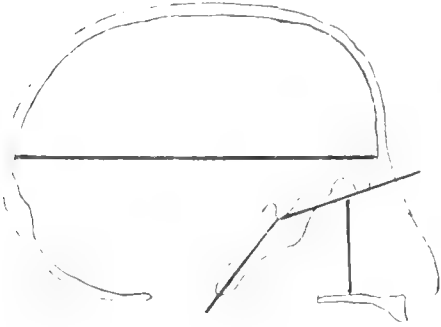


Fig. 1.

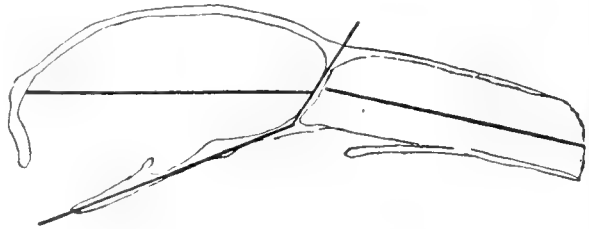


Fig. 2.

Fig. 1 shows a median section of a human skull. Fig 2 a similar section of the skull of Lemur, a Prosimia. Three lines have been drawn in both figures, viz the axis of the cranial cavity, the axis of the nasal cavity and the axis of the base of the skull. The three lines demonstrate in a simple way the essential features of the orthognathous and the prognathous skull-type. They are the following: In the orthognathous type the axis of the nasal cavity is approximately perpendicular to the axis of the cranial cavity, in other words the nasal cavity is situated beneath the cranial cavity; in the prognathous type, on the contrary, the axis extends more or less in the same direction as the axis of the cranial cavity. As to the axis of the base of the skull, it is flexed in either case, but in opposite direction. In the orthognathous type it is flexed between the basi- and the praesphenoid, an angle is formed with its open side turned anteriorly downwards. It is known in the literature as the sphenoidal angle. In the prognathous type the base is flexed between the praesphenoid and the ethmoid. An angle is formed with its open side turned posteriorly upwards. This angle I shall term the ethmoidal angle.

So it appears that the typical differences between the orthognathous and the prognathous skulls consist in the different situation of the nasal-cavity, either subcerebral or praecerebral, and in the different direction in which the base of the skull is flexed. The length of the jaws I do not consider as a fit criterion.

Now, when we test the skulls of the various classes of mammals by the criteria just mentioned, it appears that the whole class of the Primates, so not only man, is characterized by an orthognathous skull, in contradistinction to all the other mammalian classes. Applying the degree of prominence of the jaws as a criterion for prognathism is an erroneous method, which e.g. has led to the classification of apes among the prognathous forms. Though their jaws may be ever so much developed, the base of the skull never presents an ethmoidal angle, while the nasal cavity is never situated before the cranial cavity and in younger individuals there is even a sphenoidal angle. The strongly developed facial part of the skull in several apes, however, reminds us forcibly of a prognathous skull. These forms I will, therefore, distinguish as pseudopognathous.

In the foregoing the principle has been established for an inquiry into the relation between prognathism and orthognathism. The object of such an inquiry must be the answer to the question: which skull-type is the primitive one and which is the specialized type. First of all I will report the result of my examination of embryos of a number of mammals. It is the following: the fetus of all mammals is initially orthognathous, i.e. has a sphenoidal angle lacks an ethmoidal angle and the nasal cavity is subcerebral. Now, whereas this condition persists in apes partly and in man completely, in the other mammals the fetal orthognathous skull passes gradually into the prognathous type; first the sphenoidal angle disappears, then the ethmoidal angle is developed and coincidentally the nasal cavity rotates; its subcerebral position passes into a precerebral position. So it becomes evident that the orthognathous condition in man, which is the special feature of the human physiognomy, reveals itself again as a persisting fetal property.

Before demonstrating this in a series of embryos, I will briefly dwell on the fact that this transformation of the orthognathous skull into the prognathous type is a process with which we are confronted already in Reptiles, so that it has evidently been inherited by the Mammals from their reptilian ancestors.

Fig. 3 represents a median section through the head of an embryo of *Lacerta*, length of the head 4 mm. The chorda is still present, the vertebrae are not differentiated, likewise the cranio-vertebral joint is still incomplete. Of the chondrocranium the basicranial plate enclosing the Foramen can be recognized. This plate extends frontad as far as the Hypophysis cerebri, which is still attached to the epithelium of the roof of the mouth. In front of the Hypophysis lies the prechordal plate. The latter presents two enlargements the one

turned upwards: the septum orbitale, and the other turned down: the septum nasale.

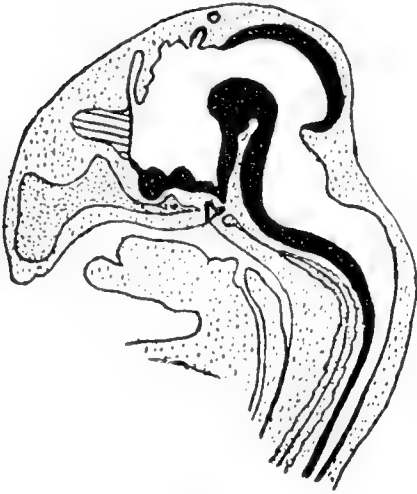


Fig. 3.

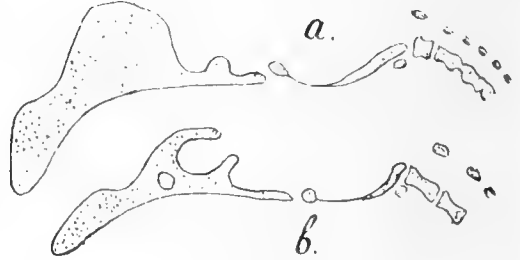


Fig. 4.

Now, two things should be observed: First that the prechordal plate extending in front of the Hypophysis, forms an angle with the basicranial plate behind it. This angle which is still more distinct in younger embryos, is identical with the sphenoida angle, the typical feature of the orthognathous human skull. The second thing to be observed is the direction of the septum nasale. In this young *Lacerta* embryo the axis of this septum is perpendicular to the base of the skull, which also is a typical feature of the orthognathous human skull. In passing, I wish to point out that in this phase of development the entrance to the mouth is, in *Lacerta*, not apical, but points downward. This reminds us incontinently of the permanent condition in *Plagiostomes*.

So the verticality of the septum nasale is a characteristic which, in this phase of development, the head of the *Lacerta*-embryo has in common with the orthognathous type. Fig. 4 shows how this type passes into the prognathous. In fig. 4^a the median section through a primordial cranium is given, head length 4.5 mm. In fig. 4^b the same with a length of 5 mm.; the enlargement in the two figures differs. Relative to the younger stage, the septum orbitale in the embryo with a head length of 4.5 mm. is considerably enlarged. It is clear that the axis of the nasal septum is no longer perpendicular to the base of the skull, but has rotated anteriorly. In the 5 mm. embryo this rotation is so considerable that the axis of the septum nasale is nearly on a level with the base of the skull. In this older embryo the septum orbitale exhibits marked signs of

resorption. So the figures 3 and 4 illustrate a rotation of the septum nasale, and consequently of the facial skull. From its original sub-cerebral position (orthognathism) it shifts into a precerebral position (prognathism). That in connection with this rotation plagiostomy changes into teleostomy we will pass over in silence, although this phenomenon would give ample scope for interesting observations.

It has thus been shown that the chondrocranium of Reptiles, in its early phase of development, resembles the orthognathous type. Now we are going to demonstrate that the process of development in Mammals bears a great resemblance to that of Reptiles. I have studied the ontogenesis of the skulls of a number of Mammals, and in all of them I met with the phenomena that I am going to describe for the skull of *Mus decumanus*.

Fig. 5 represents the median section of an embryo of *Mus decumanus* of 11.5 mm. In this stage the primordial cranium is



Fig. 5.

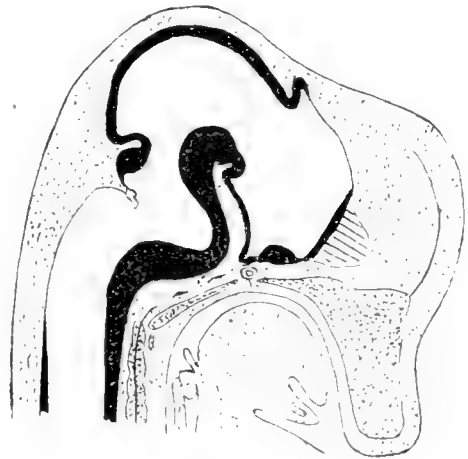


Fig. 6.

sufficiently differentiated. We will confine ourselves to the skeleton, omitting all further remarks that the following series of figures might suggest. In this stage the Hypophysis has become a closed vesicle, which, however, still adheres to the epithelium of the mouth. Behind the Hypophysis lies the basicranial plate, which in *Mus* is subchordal over its whole length. Frontal to the Hypophysis lie the prechordal plate presenting a slight broadening dorsad, which is homologous with the strongly developed Septum orbitale in Reptiles. At its lower surface the Septum nasale is fastened. There is no denying that the basicranial plate and the prechordal plate form an angle. This

angle, which we also found in *Lacerta*, is the sphenoidal angle that we know to be the typical feature of the orthognathous skull. Whereas the base of the skull is directed almost quite horizontally, the axis of the septum nasale is directed perpendicularly. Therefore in this stage of development the nasal cavity of *Mus* is subjacent to the cranial cavity. The skull of this young embryo of *Mus* possesses, therefore, two features, which are characteristic of the orthognathous skull, viz. a sphenoidal angle and a subbasal situation of the nasal cavity. That the latter condition is not the consequence of the intense development of the cerebral hemispheres, is borne out by the fact that in an early stage of development of Reptiles we find the same direction of the septum nasale. The condition in *Mus*, just described, is inherited from the reptilian ancestors of Mammals, which in their turn have inherited it from more primitive vertebrates. Plagiostomy, to which we referred heretofore, and which, to some extent, is encountered in the represented embryo of *Mus*, indicates in what direction we have to look for an explanation of this condition.

Accordingly we conclude that orthognathism is the characteristic of the young fetal mammalian skull. Now let us see how the prognathous type is developed from the primitive type.

Fig. 6 illustrates the median section through the head of an embryo of 13.5 mm. in length. The chorda begins to disappear, the Hypophysis lies within the cranial cavity, but is still attached to the mouth-epithelium. The base of the chondrocranium begins to stretch, but the sphenoidal angle is still recognizable. The axis of the septum nasale is still perpendicular to the prechordal plate.

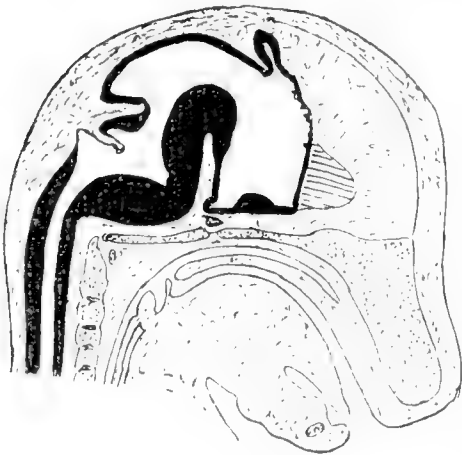


Fig. 7.

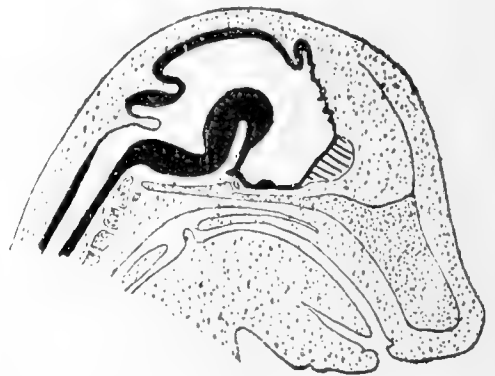


Fig. 8.

Fig. 7. Embryo of 20 mm. The basis cranii is stretched, the

sphenoidal angle has disappeared. The axis of the nasal septum is no longer vertical to the base of the skull, it has rotated, so that it forms an angle of 115° with the axis of the base of the skull.

Fig. 8. Embryo of 25 mm. The canalis Hypophyseos is closed, basal plate and prechordal plate have coalesced completely. The septum nasale has rotated further, and is inclined to the base of the skull at an angle of 130° , the part of this base to which the septum nasale is attached is bent slightly upwards, which is the first indication of the developing ethmoidal angle.

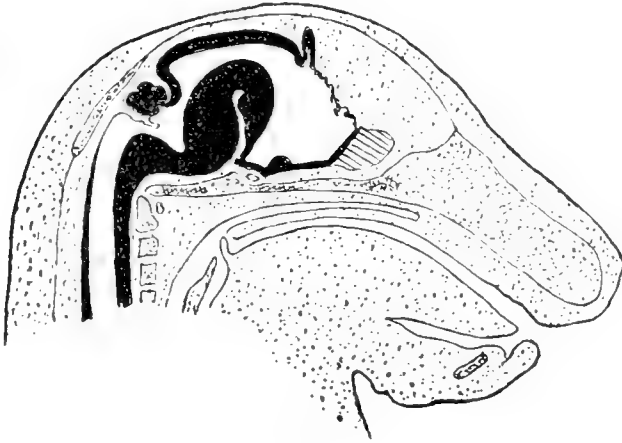


Fig. 9.



Fig. 10.

Fig. 9. Embryo of 35 mm. Three centra of ossification have appeared in the basis cranii for the Basisoccipitale, the Basisphenoid

and the Alisphenoid. The rotation of the septum nasale has continued; the nasal cavity now lies obliquely under and anteriorly to the cavum cranii. This rotatory movement apparently results from the further upward flexing of the frontal part of the basis cranii. The ethmoidal angle now becomes distinctly visible, right in front of the centrum of ossification of the Alisphenoid.

Fig. 10. Embryo of 43 mm. The ethmoidal angle has reached its definite value for the skull of the adult rat, the frontal part of the basis cranii has now become the anterior wall of the cranial cavity, the nasal cavity is situated before the cranial cavity, the skull has become prognathous.

It is evident, then, that the transformation from the orthognathous into the prognathous skull-type in the mammalian embryos is a regular process in which two succeeding phases are recognizable. In the first phase a straightening of the basis cranii takes place; the sphenoidal angle disappears. Its disappearance it attended with a change in the direction of the septum nasale, which is now placed obliquely to the base of the skull. After this the second fundamental alteration in the basis cranii commences, viz. the formation of the ethmoidal angle, the anterior (ethmoidal) portion of the base being turned up together with the septum nasale, which is attached to it. Consequently a part of the base of the fetal skull becomes the front wall of the cranial cavity.

I shall not enter into details concerning the various mammalian embryos that I have examined but will only add a few general remarks.

From the foregoing it is sufficiently evident that the orthognathous skull of man is to be considered as a persisting early fetal form. In stating this fact we have at the same time disproved the current opinion, that the sphenoidal angle, which is so characteristic of the human skull, is due to the intense development of the human brain. This angle, indeed, is not only a feature of all fetal mammalian skulls, but it occurs even in the chondrocranium of Reptiles. It is an essential character of, let me say, the primordial cranium of vertebrates in general. I shall not discuss this point any further.

The question now arises whether the intense growth of the Hemispheres has had no influence whatever on the anatomical relations of the skull, apart from the necessarily considerable enlargement of the cerebral crane. Such an influence, and even a very remarkable one, can indeed be demonstrated, as may be seen in comparing Fig. 11 and 12.

Fig. 11 shows the median section through the head of a dog's

fetus; length 32 mm.; Fig. 12 that of a human fetus 40 mm. long. The peculiarity I wish to lay stress on, regards the insertion of the



Fig. 11.

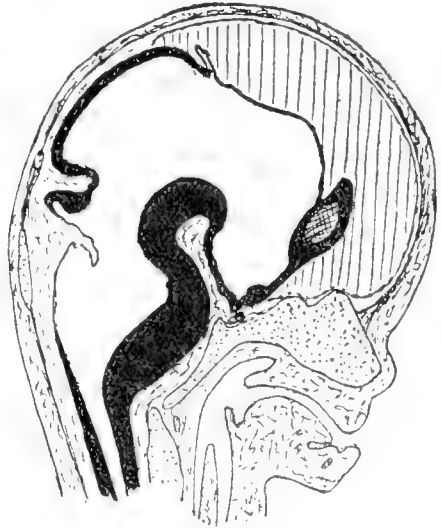


Fig. 12.

membranous vault of the crane on the cartilaginous nasal capsule. In the dog the former attaches itself to the acute border where the cranial base bends round in the nasal capsule, i.e. to the anterior margin of the cranial base. In man, on the other hand, it attaches itself in consequence of the intense development of the Hemispheres, to the anterior surface of the nasal capsule. It is obvious that a comparatively large portion of the nasal septum is hereby enclosed in the cranial cavity. This fact elucidates several phenomena observable at the human skull, I will only name them parenthetically. The shifting of the insertion of the membranous cranium to the anterior surface of the cartilaginous nasal capsule accounts for the occurrence of the *Crista galli*. This process, which is lacking in prognathous skulls is merely the top part of the nasal septum and the apex of the *Crista galli* indicates consequently the original frontal boundary of the base of the skull. This transference of the insertion of the membranous vault causes a shortening of the frontal part of the nasal region in man and it is quite obvious that the human physiognomy has been largely influenced by it. Earlier comparative anatomical inquiries already led me to conclude that the top part of the nose in Primates was reduced, and that the present boundary between nose and vault of the skull is of a secondary nature¹⁾. The

¹⁾ Die Herkunft der Fontanella metopica beim Menschen Anat. Anz. Ergänzungsheft. Bnd 38. Jena 1911.

suture between nasal and frontal bones was lying on the forehead at the spot where in man not seldom the so-called *Funiculus metopicus* is situated. The results of the embryological research lend support to this view.

Another phenomenon explained by this transference of the insertion of the membranous vault on the nasal capsule is the intra-orbital situation of the entrance to the lacrimal duct. In the half-apes this opening is extra-orbital; in the apes, on the other hand, it is taken up in the medial wall of the orbit together with the *os lacrymale*, in consequence of the shortening of the facial part of the skull in this region.

It appears then that through this transference of the insertion of the membranous vault to the anterior surface of the nasal capsule in consequence of the intense development of the cerebral hemispheres, we are able to interpret in a simple way three apparently heterogeneous phenomena, viz. *Crista galli*, *Funiculus metopicus*, and intraorbital position of the lacrimal foramen. In this connection I may still add a remark about the other Primates. We have stated that apes, however much their jaws may project, possess in reality an orthognathous skull like that of man; they are to be classed as pseudopognathous. The persistence of the subcerebral position of the nasal cavity, also in apes, is the reason why the human physiognomy is ever more or less discernible in apes, which is to be ascribed chiefly to the position of the eyes. Originally the eyes of all mammalian embryos are disposed on the lateral surface of the head. In the prognathous type, in which the nasal cavity rotates before the cranial cavity the eyes retain their lateral position. In the orthognathous type, on the contrary, in which the nasal cavity persists under the cranial cavity the eyes can draw nearer to each other, and instead of the nasal cavity the orbitae occupy a precerebral position. Now this rotation obtains with all Primates, and this is why, physiognomically, apes resemble man.

In conclusion another point of similarity is the fact that all Primates possess a *Crista galli*, so in all of them the insertion of the membranous vault of the crane is transferred to the nasal capsule under the influence of the intense growth of the cerebral hemispheres, which is proved also by the intraorbital position of the foramen lacrymale in this class of mammals.

ERRATUM.

In these Proceedings Vol. XXV nos. 5 and 6, p. 202, line 15 from the bottom, to replace "*with respect to time*" by "*with respect to TEMPERATURE*".

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TE AMSTERDAM.

PROCEEDINGS

VOLUME XXV

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Physics. — “*The Magneto-Thermic Effect according to Thermodynamics*”. (Supplement N^o. 47 to the Communications from the Physical Laboratory at Leiden). By Prof. J. P. KUENEN †.

(Communicated at the meeting of December 30, 1922).

In experiments with ferro-magnetic substances WEISS and PICCARD ¹⁾ found that the heat-effect which accompanies a magnetic change, assumes a relatively large value in the neighbourhood of the Curie-point. According to them this phenomenon, just as the discontinuity in the specific heat at the Curie-point ²⁾, is a consequence of the “molecular field”, which plays a prominent rôle in WEISS’ theory of ferro-magnetism.

It is natural to apply equations to this phenomenon which ensue from the second law of the theory of heat. The question suggests itself whether this is allowed, as non-reversible changes occur in ferro-magnetism. Every condition — leaving disturbances out of account — is indeed a condition of stable equilibrium, but in general the substance cannot pass through a definite series in both directions. This difficulty may be obviated by considering only those conditions that arise under the influence of strong mechanic or electric vibrations: these neutralize hysteresis, and with it also remanent magnetism, and the conditions then become reversible. The results obtained by the aid of thermodynamics, will in main lines most likely also hold for the phenomena occurring under normal circumstances: above the Curie-point they are, of course, strictly valid.

The external work of a magnetized system being represented by $-H d\sigma$, where H and σ denote resp. the magnetic force and the magnetisation, the chief equation of thermodynamics is:

$$d\varepsilon = T d\eta + H d\sigma \dots \dots \dots (1)$$

As it is most convenient if H is an independent variable, we write:

$$d(\varepsilon - H\sigma) = T d\eta - \sigma dH \dots \dots \dots (2)$$

from which follows:

¹⁾ P. WEISS et A. PICCARD, J. de Phys. (5) 7, p. 103, 1917.

²⁾ P. WEISS, A. PICCARD et A. CABRERA, Arch. de Genève 1917; J. de Phys. (5) 7, p. 87, 1917.

$$\frac{\partial T}{\partial H_\sigma} = -\frac{\partial \sigma}{\partial H} = -\frac{T}{c_H} \frac{\partial \sigma}{\partial T_H} \dots \dots \dots (3)$$

Here c_H is the specific heat for constant field. This equation shows that the thermic effect in question is greatly dependent on $\frac{\partial \sigma}{\partial T_H}$, hence becomes abnormally high in the neighbourhood of the Curie-point, and this is what we intended to prove.

$\frac{\partial \sigma}{\partial T}$ being < 0 , the temperature increases during the magnetisation, and reversely. According to the above-mentioned experiments c would suddenly assume a lower value at the passing of the Curie-point in upward direction, but this does not affect the conclusion drawn. The relation found is independent of WEISS' hypotheses, and sets forth the inter-relation between heat-effect and disappearance of ferro-magnetism more clearly than the equations given by WEISS and PICCARD.

When, with WEISS and PICCARD, σ is taken as independent variable, the following is found from (1):

$$\frac{\partial T}{\partial \sigma_\sigma} = \frac{\partial H}{\partial H_\sigma} = \frac{T}{c_\sigma} \frac{\partial H}{\partial T_\sigma} \dots \dots \dots (4)$$

Above the Curie-point $\frac{\sigma}{H} (T-\theta) = C$, where θ and C are constants, so that $\frac{\partial H}{\partial T_\sigma} = \frac{\sigma}{C}$. On substitution of this in (4) an equation is obtained which also occurs in the cited paper, but which is strictly proved here without having recourse to WEISS' special theory.

It will be vainly tried to estimate the said change of the specific heat at the Curie-point purely thermodynamically. Thermodynamics gives, indeed, the change of c_H with the value of H (resp. of c_σ with σ), and the difference between c_H and c_σ , but not the dependence on the temperature in question. To find this a molecular theory like that of WEISS, is indispensable. From this an expression for the internal energy ϵ will have to be derived, and also for the c 's, because $c_\sigma = \frac{\partial \epsilon}{\partial T_\sigma}$ and $c_H = \frac{\partial \epsilon}{\partial T_H} = H \frac{\partial \sigma}{\partial T_H}$.

In connection with the preceding paper I may be allowed to add a few remarks.

The late Professor KUENEN had the intention to make a communication on the subject mentioned in the title at the Meeting of the

Royal Academy of Sept. 30 1922; a few days, however, before the meeting death took him away. Among the papers found after his death was the manuscript of the above communication, ready for the press, and a few detached sheets, on which the author tried to ascertain what follows from the equations:

$$c_H = c_\sigma + T \frac{\left(\frac{\partial \sigma}{\partial T}\right)_H^2}{\left(\frac{\partial \sigma}{\partial H}\right)_T} \dots \dots \dots (A)$$

$$\frac{c_H}{c_\sigma} = \frac{\left(\frac{\partial H}{\partial \sigma}\right)_T}{\left(\frac{\partial H}{\partial \sigma}\right)_T} \dots \dots \dots (B)$$

$$\left(\frac{\partial c_H}{\partial T}\right)_T = T \left(\frac{\partial^2 \sigma}{\partial T^2}\right)_H \dots \dots \dots (C)$$

$$\left[\frac{\partial}{\partial T} \left(\frac{c_H}{T} \right) \right]_H = \left(\frac{\partial^2 \eta}{\partial \sigma^2} \right)_H \left(\frac{\partial \sigma}{\partial T} \right)_H^2 + \left(\frac{\partial \eta}{\partial \sigma} \right)_H \left(\frac{\partial^2 \sigma}{\partial T^2} \right)_H =$$

$$= \left(\frac{\partial^2 \eta}{\partial \sigma^2} \right)_H \left(\frac{\partial \sigma}{\partial T} \right)_H^2 + \frac{c_H}{T} \frac{\left(\frac{\partial^2 \sigma}{\partial T^2} \right)_H}{\left(\frac{\partial \sigma}{\partial T} \right)_H} \dots \dots \dots (D)$$

which can be derived in a purely thermodynamic way, if they are combined with the empirical data on the course of $\sigma = \sigma(T, H)$ in the neighbourhood of the Curie-point, or with the equation:

$$\varepsilon = -\frac{n\sigma^2}{2} + f(T) \dots \dots \dots (E)$$

which is the direct consequence of the formula for the molecular field H_m used by Prof. WEISS:

$$H_m = -\left(\frac{\partial \varepsilon}{\partial \sigma}\right)_T = n\sigma \dots \dots \dots (F)$$

It seems to have been his intention to throw light on the question what suppositions are *necessary* to derive the change of the specific heat of ferro-magnetic bodies at the Curie-point.

P. E.

Chemistry. — “*Determination of the Vapour Pressure of Metallic Arsenic*”. By SHINKICHI HORIBA. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of October 28, 1922).

Arsenic is one of the most interesting elements, which should be studied from the view-point of the theory of allotropy. It is a well known fact that arsenic can exist in three kinds of modification, i. e. gray, black, and yellow; the gray modification is quite stable in a wide range of temperature, while the others are rather metastable. Although many investigations have been carried out about this important element, yet it has never been tried to define the exact lines of demarcation between these three modifications. Recently some observations of its melting point have been reported by GOUBEAU¹⁾, HEIKE²⁾, RASSOW³⁾, and some measurements of the vapour pressure of its solid phase by HEIKE, but in the case of the latter, an indirect method was used, so that the results were not very accurate. The vapour pressure of the liquid phase of this element has never been determined. On the suggestion of Professor SMITS, the author has undertaken the measurements of the vapour pressure of this element in the laboratory of the University of Amsterdam; the object of the present study is, of course, to investigate the whole system of this element, but the author is not yet in the position to complete this study, owing to the difficulties of the technics of the measurements. The present communication will only represent the results of the measurements of the vapour pressure of the gray modification and give some thermal data which can be calculated from these vapour pressure data.

The Method of Investigation.

The same method of investigation, used by Prof. SMITS and BOKHORST⁴⁾ for the study of phosphorus, was applied; a small modification, which was made in the present investigation, was that a quartz indicator of pressure was used instead of the hard glass, in view

¹⁾ Compt. rend., **152**, 1767, (1911).

²⁾ Z. anorg. chem., **117**, 147 (1921): the literature of the melting point was given in this paper.

³⁾ Z. anorg. chem., **114**, 131 (1920).

⁴⁾ Z. physik. chem., **91**, 249 (1916).

of the high melting point of arsenic. Owing to the technical difficulties of making such an indicator, its sensibility was somewhat inferior to that of the indicator made of glass, still some of the indicators which were used, could keep their sensibilities within one centimeter of mercury, being sufficient for the present purpose.

The Material.

MERCK'S metallic arsenic was used after several purifications. At first the finely powdered sample was subjected to repeated sublimation in a vacuum by the aid of a large Heraeus electric furnace, the temperature of the furnace was maintained at a little over 500° C. in the first sublimation and at nearly 600° C. in the final one. The gray modification thus prepared was again very finely powdered, and was extracted by carbon disulphide in a Soxhlet apparatus for 24 hours. A small quantity of arsenic oxide, which would still remain in the above purified sample, must be reduced by hydrogen current in the pressure indicator itself.

The Filling of the Sample in the Pressure Indicator.

About 10 gr. of the sample was placed into the bulb of a quartz indicator, and a hard glass capillary tube was introduced into the bulb of the indicator, so that the end of the capillary tube was just in the spring of the indicator. Then the indicator was heated from outside by BUNSEN burners at 500° C; during the heating of the indicator a current of purified hydrogen was passed into the bulb and its spring through the above mentioned capillary tube, so that a small quantity of arsenic oxide, which still remained in the sample, was at first sublimated and the rest of it reduced to pure arsenic. After a sufficient sublimation in this way, the remainder of the sample in the bulb became perfectly pure brilliant metallic arsenic. Then the indicator was completely evacuated and the bulb of it was sealed up. It was always observed that if arsenic was sublimated in a vacuum, even at room temperature, at first it appeared as the yellow modification, which would be soon transformed into the black modification.

The Furnace of the Pressure Measurement.

A special furnace was constructed for the purpose of keeping the indicator at constant temperature, even at very high temperature. A large iron block of 14 cm. in diameter and of 30 cm. in height was heated electrically by nichrom wire. In the middle of this iron block, a hole of 3 cm. in diameter and of 25 cm. in depth was

bored, in which the indicator and a thermoelement were placed. This furnace was available till 900°. The temperature of the furnace was measured by a HERAEUS platinum-rhodium thermoelement, which was carefully adjusted before the experiment.

The Measurement of the Vapour Pressure.

The method of the pressure measurement by an indicator is exactly the same as that applied by Prof. SMITS and BOKHORST¹⁾. The equi-

TABLE I. Vapour Pressure of the Solid Phase.

$$\frac{Q}{4.571} = 7357$$

$$C = 8.279$$

| t | p atm. (obs) | Tlogp | $\frac{Q}{4.571}$ | $\Delta \left(\frac{Q}{4.571} \right)$ | p (calc.) |
|-------|----------------|--------|-------------------|---|-------------|
| 450 | 0.026 | - 1142 | 7127 | - 230 | 0.013 |
| 500 | 0.076 | - 844 | 7244 | - 113 | 0.075 |
| 525 | 0.105 | - 620 | 7227 | - 130 | 0.094 |
| 550 | 0.222 | - 538 | 7352 | + 5 | 0.219 |
| 568 | 0.362 | - 371 | 7334 | - 23 | 0.340 |
| 592 | 0.584 | - 202 | 7363 | + 6 | 0.598 |
| 604 | 0.785 | - 92 | 7353 | - 4 | 0.777 |
| 615.5 | 0.997 | - 2 | 7357 | ± 0 | 0.997 |
| 631 | 1.395 | 131 | 7354 | - 3 | 1.387 |
| 658 | 2.392 | 353 | 7354 | - 3 | 2.377 |
| 665 | 2.717 | 401 | 7365 | + 8 | 2.729 |
| 672 | 3.035 | 456 | 7377 | + 20 | 3.189 |
| 685 | 3.906 | 567 | 7365 | + 8 | 3.983 |
| 697 | 4.85 | 664 | 7368 | + 11 | 4.96 |
| 720.5 | 6.95 | 838 | 7386 | + 29 | 7.46 |
| 741 | 9.7 | 999 | 7396 | + 39 | 10.6 |
| 758 | 13.3 | 1157 | 7378 | + 21 | 14.0 |
| 772 | 16.9 | 1281 | 7371 | + 14 | 17.4 |
| 790 | 22.3 | 1432 | 7368 | + 11 | 22.8 |
| 801 | 26.1 | 1522 | 7370 | + 13 | 26.9 |
| 809 | 30.0 | 1595 | 7363 | + 6 | 30.2 |
| 815 | 33.6 | 1662 | 7348 | - 9 | 33.0 |

¹⁾ loc. cit.

TABLE II. Vapour Pressure of the Liquid Phase.

$$\frac{Q}{4.571} = 2450$$

$$C = 3.80$$

| t | p atm. (obs.) | $T \log p$ | $\frac{Q}{4.571}$ | $\Delta \frac{Q}{4.571}$ | p (calc.) |
|-----|-----------------|------------|-------------------|--------------------------|-------------|
| 808 | 34.2 | 1658 | 2450 | ± 0 | 34.2 |
| 817 | 35.7 | 1693 | 2453 | + 3 | 35.9 |
| 830 | 38.1 | 1743 | 2448 | - 2 | 38.0 |
| 843 | 40.5 | 1793 | 2447 | - 3 | 40.2 |
| 850 | 41.6 | 1818 | 2449 | - 1 | 41.5 |
| 853 | 42.2 | 1829 | 2450 | + 0 | 42.2 |

librium between vapour and condensed phase of arsenic is not very quickly established but the heating of the furnace was so slow that there was no difficulty to measure the pressure at any desired temperature. The whole measurement of the vapour pressure of the gray modification of arsenic to its liquid phase, namely from 400° C. to 850° C., required a continuous work of more than 12 hours. The results of the vapour pressure measurement were tabulated as follows: (See Table I, page 389).

Starting from CLAUSIUS and LAPAYRON'S equation and assuming that the heat of vaporization Q , is constant, that the vapour of arsenic follows the gas law and that the volume of the condensed phase can be neglected with respect to that of the vapour, the vapour pressure would be represented by a straight line $T \log p = -\frac{Q}{4.571} + CT$.

When the value of $T \log p$, from the observed values of pressure, was plotted against temperature, a good straight line was obtained from 550° C. to 700° C. as shown in Fig. II, from which we can easily calculate $Q/4.571$ and C . The table contains in the last column the values of the pressures calculated from this equation. Above 700° C. however, the $T \log p - t$ curve shows some deviation, and the calculated values of $Q/4.571$, assuming C as a constant must deviate. The deviations become gradually smaller as the temperature rises. Some of these deviations may, of course, be experimental errors, because at high temperature a little observation error of temperature would have a great effect on the value of pressure, quite the contrary of the case at low temperature, where a little error in the measurement of pressure, owing to small value of pressure, would have a great effect upon the calculated value of $Q/4.571$. But such a deviation

as observed here depends certainly on the inapplicability of the assumptions which were used in the integration of the CLAUDIUS—CLAPAYRON equation.

In the case of the liquid phase, the observed vapour pressures

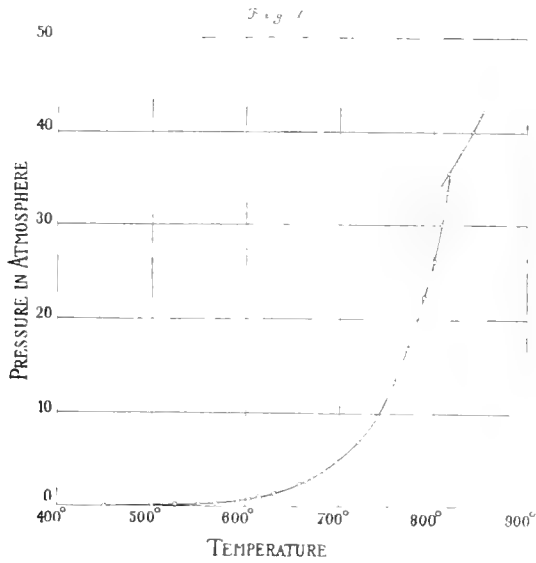


Fig. 1.

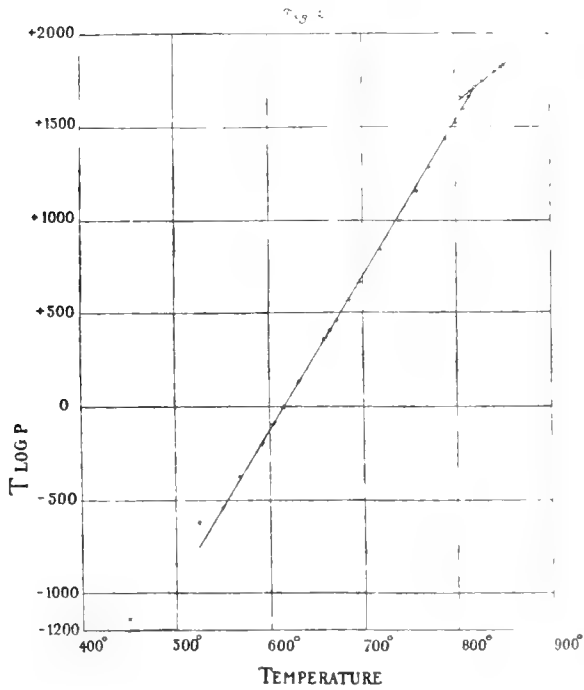


Fig. 2.

were represented quite well by $T \log p$ plotted against temperature as a straight line as seen in the table II.

The Melting Point of Arsenic.

The direct measurement of the melting point of arsenic was impossible in the course of this experiment, because the thermo-element was placed outside of the indicator.

As shown in figure I, the observed pressures¹⁾ of the gray modification very near this melting point (represented by a dotted curve) were always a little lower than the extrapolated pressure curve and at the temperatures a few degrees higher than the melting point the indicator showed the right pressure of the liquid phase. For determining the melting point I have therefore extrapolated the pressure curve of the solid phase as that of the liquid phase and it was found between **817° C.** **818° C.** which agreed well with the value given by GOUBEAU²⁾ and RASSOW³⁾. The corresponding pressure is **35.8 atm.** Of course, we could find also the value of the melting point by the intersection of the two $T \log p - t$ lines of solid and liquid phases, but in this case we find the following values.

| | | |
|---------|-----------|------|
| T | $Q/4.571$ | p |
| 822° C. | 1710 | 36.5 |

These values of the triple-point are certainly too high due to the deviation of the expression used, as was already mentioned.

As to the pressure of the triple-point, we can measure it directly with a certain degree of accuracy. Arsenic shows a very large effect of supercooling, sometimes more than 30 degrees in the authors experiments. In the case of a sudden crystallisation of such a supercooled liquid, its temperature rose very quickly to the melting point; consequently the pressure rose also suddenly several atmospheres, so that it was almost impossible to follow this sudden change of the pressure, applying the pressure outside the spring of the indicator so that, the spring broke. But if the temperature of melted arsenic was kept a few degrees below that of the melting point, and if the change of the pressure was constantly watched for a long while, sometimes longer than two hours, then it was possible to follow the sudden change of the pressure by crystallisation. In this case the pressure remained constant during the crystallisation. This adjustment of the pressure, however, requires much skill, otherwise the spring will break. In this way we could read the pressure at the melting

¹⁾ These values were not given in the table.

²⁾ loc. cit.

point, which coincided with the value found by the extrapolation of the vapour pressure curve of the solid phase to that of the liquid phase (35,8 atm.).

The Heats of Vaporization and Sublimation of Arsenic.

Heat of vaporization is, of course, a temperature function, but its temperature coefficient dQ/dt is generally negative, so that $T \log p - t$ curve should be concave to the straight line given by the expression

$$T \log p = -\frac{Q}{4.571} + CT$$

which was deduced from the assumption that Q is a constant. On the contrary, the present experimental results show that the $T \log p - t$ curve is somewhat convex to the said expression of pressure, so that we can see that the deviation of the assumption, that Q is a constant, is smaller than the total effect of deviations from other assumptions, so that we may say that the temperature coefficient of the heat of vaporization is comparatively small. It is, therefore, possible to calculate the heat of vaporization from the expression

$$T \log p = -\frac{Q}{4.571} + CT,$$

which was found to hold good for comparatively low temperatures.

For the molecular heat of sublimation we have

$$\frac{Q}{4.571} = 7357$$

hence,

$$Q_{SG} = 33.6 \text{ Kg. cal.}$$

For the molecular heat of vaporization for the liquid phase, we have

$$\frac{Q}{4.571} = 2450$$

hence,

$$Q_{ZG} = 11.2 \text{ kg. cal.}$$

From the difference of the above two heats of vaporization, we have the molecular heat of fusion

$$Q_{SL} = 22.4 \text{ kg. cal.}$$

According to TROUTON'S law, LE CHATELIER showed, that the quotient Q/T , where Q is the heat of sublimation at sublimation temperature under one atmosphere and T is the sublimation temperature, would be 30 for all substances. In the case of arsenic, the temperature of sublimation is 616° C. or 889 in absolute unit, then

$$\frac{Q}{T} = \frac{336 \times 10^3}{889} = 37.8.$$

This is a very high abnormal value, just as in the case of phosphorus.

The Black Modification of Arsenic.

It was tried to measure the vapour pressure of the black modification by means of the same indicator as was used in the above experiments. But when the vapour pressure was high enough to measure by this indicator, all the sample in it was transformed into the gray modification¹⁾, so that it was necessary to find a suitable negative catalyser for this transformation, which would not disturb the pressure measurement. The author hopes to continue this study on a future occasion.

S U M M A R Y.

The vapour pressure of the gray modification of arsenic and its liquid state were measured. From these data, the molecular heat of sublimation, of vaporization and of fusion were calculated.

In conclusion, the author expresses his cordial thanks to Professor A. SMITS for his kind suggestion and for the excellent advice he has given during the work.

Amsterdam, July 15, 1922.

¹⁾ LASCHTSCHENKO, (J. chem. Soc., 121. 972 (1922)) gave some remarks on polymorphism of arsenic from the measurement of heat evolved on cooling.

Bio-chemistry. — “*On the Influence of the Composition of the Food on the Calcium output*”. By Prof. B. SJOLLEMA. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated at the meeting of November 25, 1922).

In my experiments on the influence of cod-liver oil on calcium-, and phosphorus metabolism I found that the economizing effect of cod-liver oil on calcium and on phosphorus, was attended with a decreased production of faeces¹⁾. The question naturally arose whether, conversely, an augmented production of faeces should result from an increase in the faecal output of calcium and of phosphorus.

The answer to this question is of great importance with regard to our understanding the metabolic phenomena and the physiology of the formation of faeces. The question may be looked at also from a practical point, especially because in experiments with milk-cattle results were repeatedly obtained of late years, which render it highly probable that among the dietetic factors the mineral components are often in the minimum.

In the experiments described below we observed especially the influence of the increase of the quantity of indigestible foodstuffs (ballast) on the calcium- and phosphorus-metabolism. Two ballast-experiments have been performed this summer, both with rabbit III, which since November 1921, was always used for metabolic experiments, and which for chief diet was given a ration of dextrin, lactose, oatstraw boiled with acid and alkali, a calcium-free salt-mixture, a pure protein, viz. casein (afterward partly substituted by gluten of wheat) and a few grammes of butter.

Besides this food-mixture, wheat (whole kernels) was given in the ratio 3 mixture to 1 wheat. In addition almost always 15 grms of cabbage was administered per day. For some weeks the boiled oatstraw was replaced by sawdust boiled with acid and alkali and the cabbage by mangels or carrots.

The calcium-determinations²⁾ were made, after destruction of the urine or the faeces, titrimetrically after Mc CRUDDEN, as well as nephelo-

¹⁾ Jubilee-Volume ZWAARDEMAKER. Arch. néerl. de Physiol. t. VII, 1922.

²⁾ The analyses were performed by Miss J. E. VAN DER ZANDE, conservatrix, and by Messrs H. HOOGHOUT, analyst and H. GIETELING (volontaire).

metrically after LYMAN. The phosphorus-content was determined (also after destruction) nephelometrically and also colorimetrically, after BELL and DOISY's method altered by Briggs.

Both ballast-experiments consisted of: an initial, and a final period, each of a fortnight, in which the food-mixture contained 3% ballast; intermediate periods of a week, in which the ballast was raised to 15%, respectively lowered to 3%, and the experimental periods proper, each lasting a fortnight. In the first ballast-experiment there were three experimental periods proper, the middle one with an increased protein-content (10% gluten of wheat) and cystin. During this experiment 40 mgrms of Ca. (as Ca acetate) was given separately per day, but only 15 mgrs in the final period. In the second ballast-test calcium was administered separately to such an amount (at the most, 12.7 mgrms per day) that the calcium-content of the food was the same all through the experiment.

As the diet (without cabbage) was composed of 3 parts of the food-mixture and 1 part wheat, it contained less than 15% oat-straw, viz. $11\frac{1}{4}\%$.

With a heightened percentage of ballast or protein, the procentic amount of dextrin plus lactose in the food-mixture was lowered in both experiments.

The food was always made into a pap with boiling distilled water. The green-fodder, and in other cases the calcium-acetate was administered separately. The animal was weighed every three days. The weight varied from 3530 to 3570 grammes. The average amounts per day of calcium given off in the faeces and present in the food in the various periods of the two ballast-experiments are expressed in mgr. Ca in the following table:

| | | Initial-period 3% ballast | Experimental- period 15% ballast | Final-period 3% ballast |
|--------|----------|------------------------------|--|----------------------------|
| Output | 1st exp. | 30.4 | 88.4 en 69.3 | 12.5 |
| | 2nd exp. | 44.1 | 66.76 | 21.1 |
| Intake | 1st exp. | 59.— | 76.— | 46.3 |
| | 2nd exp. | 33.6 | 35.— | 36.4 |

It appears distinctly from both experiments that the calcium-output in the faeces is increased. The ratio of the output in the initial period to that in the experimental period in the first experi-

ment is about 100 : 250; in the second experiment the ratio is about 100 : 150.

That in the one experiment the rise of the calcium-output differed from that in the other, is no doubt due to the very different amounts of calcium administered along with the ingested food.

The extra-ballast in the experimental period as compared with the initial-period (12% of the fodder-mixture) amounted in the first experiment to about 19 mgrms per day; in the second (when no sawdust plus straw, but only straw was given as ballast) to only 9.4 mgrms. The increase of the faecal calcium-output is therefore, much larger than the amount of calcium present in the extra-ballast. That the calcium in the faeces was only for a small part derived directly from the food is also clear from the fact that especially in the second experiment the faeces contained almost twice the amount of calcium present in the ingested food.

The increase of the amounts of faeces (air-dried) that were produced in the ballast periods, was very large.

The subjoined table gives the production in grammes.

| | Initial-periods | Experimental-periods | Final-periods |
|----------|-----------------|----------------------|---------------|
| 1st exp. | 5.62 | 11.9 and 10.5 | 3.35 |
| 2nd exp. | 3.62 | 7.72 | 3.85 |

The 12% extra-ballast in the experimental periods averaged per day in the first experiment about 6.6 grms, in the second 4.7 grms. These values do not differ much from those showing the increments of the faeces production.

In the first experiment the calcium-contents of the faeces (air-dried) were considerably higher during the ballast-periods than in the initial-period; they were lowest in the final-period. (This is most likely due to the smaller quantity of calcium-salts that were administered). In the second experiment the calcium-content of the faeces diminished after the initial-period, which is not surprising if we consider the very great losses and the consequent highly negative balance. In the second experiment the difference between the output and the calcium in the food was about double the difference of the first.

The negative balance is no doubt also answerable for the fact that in the final-period of the second experiment the metabolism of calcium was much more economical than in the initial-period.

Whereas in either period the amount of calcium administered was nearly equal, the output in the initial-period was about three times that of the final-period. When comparing the values of the fore-period and of the experimental period of the second experiment, we see that whereas the quantity of faeces was about the double, the Ca-loss in the faeces was about $1\frac{1}{2}$ times greater than in the initial-period.

The calcium-output via the kidney was in the first experiment during the ballastperiods higher than in the initial- and final-period; in the second experiment there was a gradual decrease of calcium in the urine. This is also most likely attributable to the highly negative balance.

The figures warrant the assumption of a rise of the calcium-output in the urine resulting from a great amount of ballast, if the diet is not too poor in calcium. The quantity of calcium in the faeces was as a rule at least double the quantity of that in the urine.

Regarding the influence of ballast on the phosphorus output we only wish to observe that it was not quite parallel to the influence on the calcium-output. In the ballast-periods the phosphorus-content of the faeces decreased considerably in both experiments.

In a subsequent paper I intend to discuss the nitrogen-, and the iron-outputs in these experiments, and to give the results of the experiments in which we examined the influence of the alkali metals in the food on the calcium- and the phosphorus metabolism.

From the experiments here described it appears:

1. that an increase of the amount of indigestible matter in the food causes a greater loss of calcium via the intestinal canal.
2. that not all the calcium present in the faeces is necessarily derived directly from the food: a large portion of it may be given off by the organism, from which we may conclude that calcium plays a rôle in the production of faeces.
3. that in view of this it is only under certain conditions that an examination of the faeces can show whether in the food or in a part of it (e.g. calcium-salts) calcium occurs in an available form.
4. that in animals, yielding much milk, feeding with much ballast enhances the danger of a negative calcium balance.

*(From the Chemical Laboratory of the Utrecht
Veterinary University).*

Physics. — “*On Heats of Mixing of Normal and Associating Liquids.*” By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of November 25, 1922).

5. Some Remarks. Before proceeding to the case of anomalous components we will make a few remarks.

a). So far we have always written n_1 and n_2 for the molecule values. But often $n_1 = 1-x$ and $n_2 = x$ is put, so that $n_1 + n_2 = 1$. The differential quotients of w with respect to n_1 and n_2 can then also be calculated by the differential quotient with respect to x by means of the equations

$$w_1 = \frac{\partial \omega}{\partial n_1} = w - x \frac{\partial \omega}{\partial x} \quad ; \quad w_2 = \frac{\partial \omega}{\partial n_2} = w + (1-x) \frac{\partial \omega}{\partial x}.$$

This immediately follows from $w = n_1 w_1 + n_2 w_2$ and

$$\frac{\partial \omega}{\partial x} = \frac{\partial \omega}{\partial n_1} \frac{dn_1}{dx} + \frac{\partial \omega}{\partial n_2} \frac{dn_2}{dx} = -\frac{\partial \omega}{\partial n_1} + \frac{\partial \omega}{\partial n_2} = -w_1 + w_2.$$

The same thing, of course, holds not only for w , but for every homogeneous function of the 1st degree with respect to the molecular values n_1 and n_2 (e.g. v).

For a homogeneous function of the 0th degree with respect to n_1 and n_2 (e.g. w_1, v_1 , etc.; the degree of dissociation of the double molecules β (see further), etc.) we have:

$$\frac{\partial \beta}{\partial n_1} = -x \frac{\partial \beta}{\partial x} \quad ; \quad \frac{\partial \beta}{\partial n_2} = (1-x) \frac{\partial \beta}{\partial x},$$

which follows from:

$$n_1 \frac{\partial \beta}{\partial n_1} + n_2 \frac{\partial \beta}{\partial n_2} = 0 \quad \text{and} \quad \frac{\partial \beta}{\partial x} = -\frac{\partial \beta}{\partial n_1} + \frac{\partial \beta}{\partial n_2} \quad (\text{see above}).$$

b). We have seen that when $v_1^0 \sqrt{a_1} - v_2^0 \sqrt{a_1} = 0$ (i.e. when the critical pressures of the two components are the same) Δv becomes = 0 according to (3) (hence also Δv_1 and Δv_2). But according to (1) then also $w = 0$ (and this holds also for w_1 and w_2).

Now

$$v = v_0 + \Delta v = n_1 v_1^0 + n_2 v_2^0 + \Delta v.$$

hence when $\Delta v = 0$, simply :

$$v = n_1 v_1^0 + n_2 v_2^0 \quad ; \quad v_1 = \frac{\partial v}{\partial n_1} = v_1^0 \quad ; \quad v_2 = \frac{\partial v}{\partial n_2} = v_2^0,$$

so that then v becomes a *linear* function of x , viz. $v = v_1^0 + x(v_2^0 - v_1^0)$.

In the supposed case also the following equation may be written (see § 2) :

$$\frac{a}{v} = \frac{a}{v_0} = n_1 \frac{a_1}{v_1^0} + n_2 \frac{a_2}{v_2^0},$$

hence also

$$T_k = n_1 T_{k_1} + n_2 T_{k_2},$$

i.e. the *critical temperature* of the "ideal" mixture is also a *linear* function of x , viz. $T_k = T_{k_1} + x(T_{k_2} - T_{k_1})$.

For $a'_{1,2}$ holds:

$$\frac{a}{v^2} = \frac{a}{v_0^2} = \frac{(n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2}{(n_1 v_1^0 + n_2 v_2^0)^2} = \frac{a_1}{v_1^0{}^2} = \frac{a_2}{v_2^0{}^2},$$

when $\sqrt{a_1}/v_1^0$ is $= \sqrt{a_2}/v_2^0$ in consequence of the equality of the critical pressures. In ideal mixtures the *critical pressure* remains, therefore, constant $= p_{k_1} = p_{k_2}$, whatever is the value of x .

6. Associated components.

For the calculation of w we can adopt the whole derivation of § 2 unchanged; it should only be borne in mind that, the degree of dissociation of the double molecules of the components being β_1 and β_2 in the mixture, that of the *pure* components will be different, viz. β_1^0 and β_2^0 . Thence

$$(n_1 e'_1 + n_2 e'_2) - (n_1 e'_1 + n_2 e'_2)_0$$

will not be $= 0$ now. For we can write e.g.

$$e'_1 = \frac{1-\beta_1}{2} (e'_1)_d + \beta_1 (e'_1)_e = (e'_1)_{\frac{1}{2}d} + \beta_1 \{ (e'_1)_e - (e'_1)_{\frac{1}{2}d} \} = (e'_1)_{\frac{1}{2}d} + \beta_1 q_1,$$

when $(e'_1)_d$ is the energy constant of a double molecule and $(e'_1)_e$ of a single molecule. A similar expression applies to e'_2 . Here e'_1 and e'_2 always refer, therefore, to single molecular quantities. The quantities q_1 and q_2 are the "pure" heats of dissociation, i.e. without the parts referring to the volume contraction (see further below). For the above expression the following equation may, therefore, be written :

$$n_1 (\beta_1 - \beta_1^0) q_1 + n_2 (\beta_2 - \beta_2^0) q_2 = q.$$

Further it should be borne in mind that a remains unchanged on dissociation, for on simple joining of two single molecules to one double molecule, \sqrt{a} will likewise become twice as great;

hence v/a will have the same value for $1/2$ double molecule as for 1 single molecule.

The same thing is assumed with regard to the heat capacities k_1 and k_2 . There too — especially for larger molecules — no contraction of the value is supposed.

Thus instead of (1) the following form is found:

$$w = q + n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0 v_1^0 v_2^0} + \left(p + \frac{a}{v v_0} \right) \Delta v \quad (1_{ass.})$$

The values of w_1 and w_2 are found in an entirely analogous way as in § 2, viz. from (cf. equation (1^a)):

$$w = q + n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2} + \left(p + \frac{a_1}{v_1 v_1^0} \right) n_1 \Delta v_1 + \left(p + \frac{a_2}{v_2 v_2^0} \right) n_2 \Delta v_2,$$

in which further:

$$\begin{aligned} \frac{a_1}{v_1 v_1^0} \Delta v_1 - \frac{a_1}{(v_1^0)_{\beta_1^0}} - \frac{a_1}{(v_1)_{\beta_1}} &= \left(\frac{a_1}{(v_1^0)_{\beta_1^0}} - \frac{a_1}{(v_1)_{\beta_1^0}} \right) + \left(\frac{a_1}{(v_1)_{\beta_1^0}} - \frac{a_1}{(v_1)_{\beta_1}} \right) = \\ &= \frac{a_1}{(v_1^0 v_1)_{\beta_1^0}} (v_1 - v_1^0)_{\beta_1^0} + \frac{a_1}{(v_1)_{\beta_1^0} (v_1)_{\beta_1}} (\beta_1 - \beta_1^0) \Delta_1, \end{aligned}$$

as

$$v_1 = \frac{1 - \beta_1}{2} (v_1)_d + \beta_1 (v_1)_e = (v_1)_{\beta_1 d} + \beta_1 ((v_1)_e - (v_1)_{\beta_1 d}) = (v_1)_{\beta_1 d} + \beta_1 \Delta_1,$$

so that $(v_1)_{\beta_1} - (v_1)_{\beta_1^0} = (\beta_1 - \beta_1^0) \Delta_1$. In this Δ_1 represents the change of volume (contraction), when in the mixture $1/2$ double molecule becomes 1 single molecule.

This quantity Δ_1 can possess a considerable value. The phenomenon of the *maximum-density* of *water* e.g. finds its explanation in the great value of Δ_1 , so that below 4°C . the thermal expansion is even exceeded by the *diminution* of volume in consequence of the progressing dissociation of the double molecules. Above 4°C . the thermal expansion will predominate ¹⁾.

The same thing holds for $\frac{a_2}{v_2 v_2^0} \Delta v_2$, so that, taking into account that also

$$\Delta v_1 = (v_1)_{\beta_1} - (v_1^0)_{\beta_1^0} = (v_1 - v_1^0)_{\beta_1^0} + ((v_1)_{\beta_1} - (v_1)_{\beta_1^0}) = (\Delta v_1)_{\beta_1^0} + (\beta_1 - \beta_1^0) \Delta_1$$

$$\Delta v_2 = (v_2)_{\beta_2} - (v_2^0)_{\beta_2^0} = (v_2 - v_2^0)_{\beta_2^0} + ((v_2)_{\beta_2} - (v_2)_{\beta_2^0}) = (\Delta v_2)_{\beta_2^0} + (\beta_2 - \beta_2^0) \Delta_2$$

¹⁾ This explanation, given by me for the first time in the VAN 'T HOFF-volume of the Zeitschr. f. ph. Ch. (Bd. 31. 1899, p. 1 et seq.) more than 20 years ago (see particularly p. 12—16), is not yet found mentioned in any handbook. Except for a few favourable exceptions this is also the case with many other theories, rules and explanations given by me.

we may finally write:

$$w = n_1(\beta_1 - \beta_1^0) \left[q_1 + \left(p + \frac{a_1}{(v_1)_{\beta_1^0} (v_1)_{\beta_1}} \right) \Delta_1 \right] + \left. \begin{aligned} &+ n_2(\beta_2 - \beta_2^0) \left[q_2 + \left(p + \frac{a_2}{(v_2)_{\beta_2^0} (v_2)_{\beta_2}} \right) \Delta_2 \right] + n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2} + \\ &+ \left(p + \frac{a_1}{(v_1 v_1^0)_{\beta_1^0}} \right) n_1 (\Delta v_1)_{\beta_1^0} + \left(p + \frac{a_2}{(v_2 v_2^0)_{\beta_2^0}} \right) n_2 (\Delta v_2)_{\beta_2^0} \end{aligned} \right\}$$

In this the quantities

$$Q_1 = q_1 + \left(p + \frac{a_1}{(v_1)_{\beta_1^0} (v_1)_{\beta_1}} \right) \Delta_1 \quad ; \quad Q_2 = q_2 + \left(p + \frac{a_2}{(v_2)_{\beta_2^0} (v_2)_{\beta_2}} \right) \Delta_2$$

are the *total* (absorbed) heats of dissociation of the components in the mixture, on transition of $1/2$ double molecule to 1 single molecule. When we further write:

$$n_1 (\beta_1 - \beta_1^0) Q_1 + n_2 (\beta_2 - \beta_2^0) Q_2 = Q,$$

we get finally:

$$w = Q + n_1 n_2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v v_1 v_2} + \left(p + \frac{a_1}{(v_1 v_1^0)_{\beta_1^0}} \right) n_1 (\Delta v_1)_{\beta_1^0} + \left. \begin{aligned} &+ \left(p + \frac{a_2}{(v_2 v_2^0)_{\beta_2^0}} \right) n_2 (\Delta v_2)_{\beta_2^0} \end{aligned} \right\} (1_{ass.})$$

Taking the same remark into consideration in the differentiation as in § 2, we find from this for w_1 and w_2 :

$$w_1 = \left[(\beta_1 - \beta_1^0) Q_1 + n_1 Q_1 \frac{d\beta_1}{dn_1} + n_2 Q_2 \frac{d\beta_2}{dn_1} \right] + n_2^2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v^2 v_1} + \left. \begin{aligned} &+ \left(p + \frac{a_1}{(v_1 v_1^0)_{\beta_1^0}} \right) (\Delta v_1)_{\beta_1^0} \\ w_2 = &\left[(\beta_2 - \beta_2^0) Q_2 + n_1 Q_1 \frac{d\beta_1}{dn_2} + n_2 Q_2 \frac{d\beta_2}{dn_2} \right] + n_1^2 \frac{(v_2 \sqrt{a_1} - v_1 \sqrt{a_2})^2}{v^2 v_2} + \\ &+ \left(p + \frac{a_2}{(v_2 v_2^0)_{\beta_2^0}} \right) (\Delta v_2)_{\beta_2^0} \end{aligned} \right\} (2_{ass})$$

In the equation (1_{ass.}) we now have (see above):

$$\Delta v = v - v_0 = n_1 \Delta v_1 + n_2 \Delta v_2 = n_1 (\Delta v_1)_{\beta_1^0} + n_2 (\Delta v_2)_{\beta_2^0} + \left. \begin{aligned} &+ n_1 (\beta_1 - \beta_1^0) \Delta_1 + n_2 (\beta_2 - \beta_2^0) \Delta_2 \end{aligned} \right\} (8)$$

in which the last two terms with Δ_1 and Δ_2 will be greatly predominant. Even if the critical pressures of the two components were about the same, so that $(\Delta v_1)_{\beta_1^0}$ and $(\Delta v_2)_{\beta_2^0}$ will become = 0,

Δv will remain comparatively great, because Δ_1 and Δ_2 will retain their values.

Hence in associating components the term with Δv will still more greatly predominate in (1_{ass}) than in mixtures of normal substances, because also q_1 and q_2 will never be great. Just as with the capacities of heat, these differences in the energy constants of the half double molecules and of the single molecules will probably be even quite negligible. Even more than for non-associated components now

$$\frac{w}{\Delta v} = p + \frac{a}{v v_0} = \frac{a}{v v_0} = \frac{a}{v^2}$$

may be put, which values will again not differ much in different pairs of substances, when the critical pressures of these substances do not differ too much.

7. Approximative value of $\beta_1 - \beta_1^0$ with small values of n_2 (or x).

From the perfectly accurate equation of dissociation¹⁾ of the 1st component in the mixture, viz.:

$$\frac{(1-x)\beta_1^2}{\frac{1}{2}(1-\beta_1) \left[(1-x)\frac{1+\beta_1}{2} + x\frac{1-\beta_2}{2} \right]} = K_1 = \frac{K'_1}{p + \frac{a}{v^2}} e^{-\frac{p + \frac{a}{v^2}}{RT} \Delta_1},$$

in which K'_1 is still a function of the temperature, or also

$$\frac{\beta_1^2}{(1-\beta_1^2) \left(1 + \frac{x}{1-x} \frac{1+\beta_2}{1+\beta_1} \right)} = \frac{1}{4} K_1, \quad \text{i. e.} \quad \frac{\beta_1^2}{1-\beta_1^2} = \frac{1}{4} K_1 (1 + \varphi),$$

when $\frac{x}{1-x} \frac{1+\beta_2}{1+\beta_1} = \varphi$ is put, follows immediately:

$$\beta_1 = \sqrt{\frac{\frac{1}{4} K_1 (1 + \varphi)}{1 + \frac{1}{4} K_1 (1 + \varphi)}} = \sqrt{\frac{\frac{1}{4} K_1}{1 + \frac{1}{4} K_1}} \sqrt{\frac{1 + \varphi}{1 + \frac{1}{4} K_1 \varphi}}.$$

Here is evidently $\sqrt{\frac{\frac{1}{4} K_1}{1 + \frac{1}{4} K_1}} = \beta_1^0$ (for $\varphi=0$ when $a=0$; hence

$$\beta_1 = \beta_1^0 \sqrt{\frac{1 + \varphi}{1 + \beta_1^0{}^2 \varphi}},$$

¹⁾ See among other things Arch. Teyler XI, 3^e Partie, 1908, p. 44 et seq.

which for smaller values of x (g) passes into

$$\beta_1 = \beta_1^0 (1 + \frac{1}{2} (1 - \beta_1^{0^2}) g),$$

so that we get:

$$\beta_1 - \beta_1^0 = \frac{1}{2} \beta_1^0 (1 - \beta_1^{0^2}) g = \frac{1}{2} \beta_1^0 (1 - \beta_1^{0^2}) \frac{x}{1-x} \frac{1 + \beta_2}{1 + \beta_1}.$$

Now for small values of x we may put $\beta_2 = 1$ and $\beta_1 = \beta_1^0$, so that finally becomes in approximation:

$$(x \text{ small}) \beta_1 - \beta_1^0 = \frac{x}{1-x} \beta_1^0 (1 - \beta_1^0), \dots \dots \dots (9)$$

and $x \beta_1^0 (1 - \beta_1^0)$ may be written for $n_1(\beta_1 - \beta_1^0) = (1-x)(\beta_1 - \beta_1^0)$.

8. Reduction of the formula for w in normal components.

When we want to test the formulae derived above by some experimental data, we can only do so with mixtures of *normal* components. With regard to *anomalous* components (water, alcohol, acids, etc.) we lack the knowledge of the quantities q and Δ . On the contrary we calculated them approximately at the time (loc. cit.) from the experimental results, e.g. from the volume-contraction of water-alcohol mixtures. We must, therefore, confine ourselves, to formulae (1) and (3), and when we apply these also to abnormal components, we shall be able to find something regarding the probable values of q and Δ from the *deviations* between the calculated values and those found experimentally.

For Δv we found (cf. besides (3), also (3^a) and (3^b)):

$$\Delta v = n_1 n_2 \frac{2/7 m}{1 - 2/7 m} \frac{v_1^0 \sqrt{a_2} (1 - \tau)}{a_1 a_2} \left\{ (\sqrt{a_1} - \sqrt{a_2}) \sqrt{a_1 a_2} - \frac{1}{2} (n_1 a_1 + n_2 a_2) \frac{v_1^0 \sqrt{a_2} (1 - \tau)}{v_0} \right\},$$

when

$$\frac{v_2^0 \sqrt{a_1}}{v_1^0 \sqrt{a_2}} = \frac{b_{k_2} \sqrt{a_{k_1}}}{b_{k_1} \sqrt{a_{k_2}}} = \sqrt{\frac{p_{k_1}}{p_{k_2}}} = \tau$$

is written. Therefore, according to (1), with omission of p, w becomes:

$$w = n_1 n_2 \left[\frac{v_1^0 a_2}{v_0 v_1^0 v_2^0} (1 - \tau)^2 + \frac{a}{v v_0} \frac{2/7 m}{1 - 2/7 m} \frac{v_1^0 \sqrt{a_2} (1 - \tau)}{a_1 a_2} \right],$$

or also

$$w = n_1 n_2 \frac{a_2}{v_0} \frac{v_1^0}{v_0} \left[(1 - \tau)^2 + \frac{1}{6} (1 - \tau) \frac{a}{a_2} \frac{v_2^0}{v} \left\{ \left(1 - \sqrt{\frac{a_2}{a_1}} \right) \frac{1}{2} \left(n_1 + n_2 \frac{a_2}{a_1} \right) \frac{v_1^0}{v_0} (1 - \tau) \right\} \right],$$

when in approximation $m = T: T_k = 1/2$ is put. When $7RT_{k_2}$ is written for a_2/v_2^0 and $7RT_k$ for a_1/v_1 , and further

$$\frac{a_2}{a_1} = \frac{a_{k_2}}{a_{k_1}} = \frac{b_{k_2} T_{k_2}}{b_{k_1} T_{k_1}} = q,$$

in which $b_{k_2}:b_{k_1}$ can be calculated from $(T_{k_2}:p_{k_2}):(T_{k_1}:p_{k_1})$, we get finally:

$$w = 7 n_1 n_2 RT_{k_2} \frac{v_1^0}{v_0} \left[(1-\tau)^2 + \frac{1}{6} \frac{T_k}{T_{k_2}} (1-\tau) \left\{ (1-\sqrt{q}) - \frac{1}{2} \frac{v_1^0}{v_0} (1-\tau) (n_1 + n_2, q) \right\} \right] \quad (10)$$

When *equimolecular* quantities of the components are used, $n_1 = 1-x = 1/2$ and also $n_2 = x = 1/2$, and we get:

$$w_{1/2} = \frac{7}{4} RT_{k_2} \frac{v_1^0}{1/2 (v_1^0 + v_2^0)} \left[(1-\tau)^2 + \frac{1}{6} \frac{1/2 (T_{k_1} + T_{k_2})}{T_{k_2}} (1-\tau) \left\{ (1-\sqrt{q}) - \frac{1}{4} \frac{v_1^0}{1/2 (v_1^0 + v_2^0)} (1-\tau) (1+q) \right\} \right],$$

as $v_0 = n_1 v_1^0 + n_2 v_2^0$, and approximately $T_k = 1/2 (T_{k_1} + T_{k_2})$. The latter is strictly accurate only when the critical pressures of the two components are equal (see § 5 under *b*). When by way of abbreviation

$$\frac{v_1^0}{1/2 (v_1^0 + v_2^0)} = \lambda_1 \quad ; \quad \frac{1/2 (T_{k_1} + T_{k_2})}{T_{k_2}} = \lambda_2$$

is put, then finally with $R = 2$, so that w is expressed in gr. kal.:

$$w_{1/2} = \frac{7}{2} \lambda_1 T_{k_2} \left[(1-\tau)^2 + 1/6 \lambda_2 (1-\tau) \left\{ (1-\sqrt{q}) - 1/4 \lambda_1 (1-\tau) (1+q) \right\} \right] \quad (10^a)$$

This formula is, of course, asymmetrical on account of T_{k_2} only *in appearance*, in as much as we have placed $v_1^0 \sqrt{a_2}$ in $v_1^0 \sqrt{a_2} - v_2^0 \sqrt{a_1}$ outside the parentheses. If we had done this with $v_2^0 \sqrt{a_1}$, T_{k_1} would have appeared as fore-factor, but then $\sqrt{p_{k_1}:p_{k_2}} - 1$ would also have been substituted for $1 - \sqrt{p_{k_2}:p_{k_1}}$. We now henceforth take τ always < 1 , so that that component is chosen as the first, of which the critical pressure is *lowest*.

In consequence of the fore-factor $RT_{k_2} = 1/7 a_2/v_2^0$, w is duly of the dimension of an energy. Further only *ratios* of quantities occur in (10^a). If, therefore, the components belong to the same family of substances, e.g. to the extensive family of "ordinary" substances (critical temp. between 400° and 600° abs., $\gamma = 0,9$, $f = 7$, $r = v_k : b_k = 2,1$, etc.), the error committed by putting $v_2^0 : v_1^0 = b_{k_2} : b_{k_1}$ and $a_2 : a_1 = a_{k_2} : a_{k_1}$ in τ and q , is certainly negligible.

For the ratios in question are about the same for all these substances — provided only that they be in corresponding states (e.g. $m = 1/2$) — which will approximately be the case when the critical temperatures are not too divergent. Only in the fore-factor a_2/v_2^0 care has of course been taken by means of the factor 7 that the corrections in question are duly observed¹⁾.

As according to (1)

$$w = \Delta P + \frac{\alpha}{v v_0} \Delta v = \Delta P + \frac{\alpha}{v_0} \frac{\Delta v}{v} = \Delta P + 7R \cdot \frac{1}{2} (T_{k_1} + T_{k_2}) \frac{\Delta v}{v}$$

(see above), it immediately follows from (10^a) that

$$\frac{\Delta v_{1/2}}{v} = \frac{1}{24} \lambda_1^0 (1-\tau) \left\{ (1 - \sqrt{\varphi}) - 1/4 \lambda_1 (1-\tau) (1+\varphi) \right\}, \quad (11)$$

from which $\Delta v_{1/2}$ can be calculated ($v = 1$).

When the critical pressures of the two components are equal, then τ is $= 1$ and w and Δv both become $= 0$. As we already pointed out in our first paper, then (i.e. with very small difference of p_{k_1} and p_{k_2}) $1-\tau$ is greater than $(1-\tau)^2$, so that the part with Δv will predominate in w . But if the critical pressures differ somewhat more, the first part will continue to predominate. As will appear from the calculation in the following paragraph, the part with Δv is at most $1/5$ of the first part, but often it is much less. Hence the principal term of w remains ΔP , and this may be represented by the single formula ($x = 1/2$):

$$w_{1/2} \approx \Delta P_{1/2} = 7/4 \lambda_1 T_{k_2} (1-\tau)^2.$$

If one wants, therefore, to form an approximate idea of the value of the heat of mixing w , it will mostly be sufficient to calculate the said value of ΔP .

The value of Δv will sometimes be positive, sometimes negative. Not always are the conditions for contraction (Δv negative) fulfilled — see § 3: “As regards the sign of Δv ” etc. According to the tables on p. 160—161, 169 and 176 of KREMANN’s cited book there are about an equal number of mixtures of normal liquids with a positive as with a negative Δv . Everything, of course, depends on whether

$$(1 - \sqrt{\varphi}) - 1/4 \lambda_1 (1-\tau) (1+\varphi) > \text{of} < 0,$$

¹⁾ As $RT_k = 3/27 \lambda \cdot a_k^2/b_k$ in which λ is about $27/28$ for ordinary substances, $a_k/b_k = 7/2 RT_k$. Now a at $T = 1/2 T_k$ is about $1,4 a_k$ and $v = 0,73 b_k$, so that we have $a/v = 2 a_k/b_k = 7RT_k$.

i. e. whether (in approximation) νq is $<$ or $> 1 - \frac{1}{2} \lambda_1 (1 - \tau)$. And, of course, nothing can be said beforehand with regard to this.

9. Some numerical results.

That in case of mixing of normal substances the heat of mixing is actually $= 0$ or very slight ($+$ or $-$), when the *critical pressures are about equal*, appears among others from the following examples (compare also Table V on p. 64—65 in KREMANN'S book).

| | | | | |
|------------------------------|----------------------------------|-------------------------|--------------------------|--|
| $C_6H_5Cl - C_6H_5Br$ | $(p_k = 44,6 \text{ and } 44,6)$ | $w = 0 \text{ to } 3,3$ | (YOUNG 1903 and KR.) | |
| Dimethylaniline — m. Xylene | ($\nu > 35,8 > 35,8$) | $+ 2,8$ | } KREMANN c. s. 1914. | |
| Amylformiate — Propylacetate | ($\nu > 34,1 > 34,8$) | $- 2,0$ | | |
| p-Xylene — m-Xylene | ($\nu > 35,0 > 35,8$) | $- 2,0$ | | |
| p-Xylene — o-Xylene | ($\nu > 35,0 > 36,9$) | $+ 2,3$ | | |
| m-Xylene — o-Xylene | ($\nu > 35,8 > 36,9$) | $+ 2,0$ | | |

Of the many mixtures studied, of which the critical pressures are more or less different, we have calculated¹⁾ the following ones according to (10^a) for a comparison with the results of the observation.

1. Toluene-Benzene. Here we have:

| p_k | T_k | $T_k/p_k = \theta b_k$ | $T_k \theta b_k$ | τ | q | νq | λ_1 | λ_2 |
|-------|-------|------------------------|------------------|--------|-------|---------|-------------|-------------|
| 41.6 | 594 | 14.3 | 8490 | 0.932 | 0.774 | 0.880 | 1.10 | 1.028 |
| 47.9 | 562 | 11.7 | 6580 | | | | | |

For the calculation of $\lambda_1 = v_1^0 : \frac{1}{2}(v_1^0 + v_2^0)$ we may either take the densities at the temperature of the experiment, or — as v_1^0 and v_2^0 will be proportional to b_{k_1} and b_{k_2} — introduce the above values of θb_k (θ is a certain numerical value). We have done the latter. We now find:

$$\begin{aligned}
 w &= \frac{7}{8} \times 1,1 \times 562 (0,00462 + \frac{1}{6} 1,03 \cdot 0,068 \{ 0,120 - \frac{1}{4} 1,1 \cdot 0,068 \cdot 1,744 \}) \\
 &= 2162 (0,00462 + 0,0117 \{ 0,120 - 0,033 \}) \\
 &= 2162 (0,00462 + 0,00102) = 2162 \times 0,00564 = \mathbf{12,2 \text{ gr.cal.}}
 \end{aligned}$$

ALEXEJEW found 14,0 (from YOUNG follows 15,8, and KR. found 18,9).

¹⁾ Both in Table 5 for w (on p. 164) and in Table 23 for Δv (p. 175) the "calculated" values in KREMANN'S book are all inaccurate, because instead of the accurate formula derived by me for Δv , an approximate one was used. Besides $\frac{27}{8} RT_c$ was put in w instead of $a/v = a/b = 7RT_c$, which in itself already causes the values calculated for w to be twice too small. Etc.

It is seen that here the value of the term Δv is about 22% of the principal term.

The discrepancies between calculated and found values — also in the following examples — must be chiefly ascribed, besides to experimental difficulties and small approximations in the derivation of the formula, to the often inaccurately known values of the *critical pressures*. Even a slight error in them gives already rise to a comparatively great change in the value of $(1-\tau)^2$.

The following value is immediately found for $\Delta v/v$ according to (11):

$$\Delta v/v = 1/_{34} \times 1,1 \times 0,068 \times 0,087 = \mathbf{0,00027}.$$

The value $0,05 : 100 = 0,00050$ was found (see Table 21 on p. 160—161 and p. 175 in KR.)¹⁾.

2. **Metaxylene-Benzene.** There we have what follows.

| P_k | T_k | θb_k | $T_k \cdot id.$ | τ | φ | $\sqrt{\varphi}$ | λ_1 | λ_2 |
|-------|-------|--------------|-----------------|--------|-----------|------------------|-------------|-------------|
| 35.8 | 622 | 17.4 | 10820 | 0.864 | 0.608 | 0.780 | 1.20 | 1.053 |
| 47.9 | 562 | 11.7 | 6580 | | | | | |

This gives:

$$\begin{aligned} w &= 7/2 \times 1,2 \times 562 (0,0185 + 1/6 \cdot 1,05 \cdot 0,136 \{0,220 - 1/4 \cdot 1,2 \cdot 0,136 \cdot 1,608\}) \\ &= 2351 (0,0185 + 0,0239 \{0,220 - 0,065\}) \\ &= 2351 (0,0185 + 0,0037) = 2351 \times 0,0222 = \mathbf{52,2} \text{ gr. cal.} \end{aligned}$$

KREMANN found 57 gr. cal. The agreement is again very satisfactory (taking the above remarks into consideration). The term with Δv is 20% of the principal term. Further:

$$\Delta v/v = 1/_{24} \times 1,2 \times 0,136 \times 0,155 = \mathbf{0,00105}.$$

KR. found $0,15 : 100 = 0,00150$. The order of magnitude is the same in every case.

The mixtures with CCl_4 as component all present deviations. Now CCl_4 is certainly *associated* (see also KR., p. 68 and 140), so that this accounts for the deviations.

¹⁾ It is not very clear in KREMANN's records whether we should divide by 100, or by $1/2(v_1^0 + v_2^0) = 195,5$. (Cf. p. 175). In the latter case $\Delta v/v$ would be $= 0,00026$, in perfect agreement with the calculated value. As regards YOUNG's value, it deviates considerably from that of KREMANN. He found viz. $0,16\%$ instead of $0,05\%$, hence more than 3 times the value. Also for w there are often large differences.

Thus according to calculation the mixture $\underline{CCl_4-C_6H_6}$ ($p_k = 45,0$ and $47,9$) would have to give a heat of mixing $= + 2,0$ gr. cal., whereas $+ 21,4$ was found by YOUNG. The value of $\Delta v/v$, viz. $- 0,00130$, found by YOUNG, points to a pretty great volume contraction which, however, does not account for the too great positive value for w . Also the vapour-tension line deviates here.

The mixture $\underline{C_7H_8-CCl_4}$ ($p_k = 41,6$ and $45,0$) leads us to expect $+ 3,9$ for w , whereas w is $= - 8,5$ according to YOUNG. To this belongs $\Delta v/v = - 0,00070$ according to the same author, and accordingly w and Δv are both negative.

3. $\underline{C_7H_8Ac-CCl_4}$. The calculation of this mixture may be reproduced here. We have:

| p_k | T_k | θb_k | $T_k . id.$ | τ | q | \sqrt{q} | λ_1 | λ_2 |
|-------|-------|--------------|-------------|--------|--------|------------|-------------|-------------|
| 38.0 | 523.2 | 13.77 | 7204 | 0.9189 | 0.9543 | 0.9769 | 1.054 | 0.9704 |
| 45.0 | 556.2 | 12.36 | 6875 | | | | | |

giving:

$$\begin{aligned}
 w &= \frac{1}{2} \times 1,054 \times 556,2 (0,006577 + \\
 &\quad + \frac{1}{8} 0,9704 \cdot 0,0811 \{0,0231 - \frac{1}{4} 1,054 \cdot 0,0811 \cdot 1,9543\}) \\
 &= 2052 (0,006577 + 0,01312 \{0,0231 - 0,0418\}) \\
 &= 2052 (0,006577 - 0,000245) = 2052 \cdot 0,006332 = + 13,0 \text{ gr. cal.}
 \end{aligned}$$

YOUNG found $- 20,1$. Calculation here gives a negative value for Δv , the correction term not being even so much as 4% of the principal term. For $\Delta v/v$ we calculate:

$$\Delta v/v = \frac{1}{4} \times 1,054 \times 0,0811 \times (- 0,187) = - 0,00067.$$

The value $+ 0,00030$ was found by YOUNG. Again w and Δv (found) have opposed signs, which is strange, and renders the accuracy of YOUNG's values somewhat questionable. (Cf. also the last Footnote).

Let us now give a few examples of recognized *associated* components.

4. $\underline{C_6H_6-C_2H_5OH}$. We have in this case:

| p_k | T_k | θb_k | $T_k . id.$ | τ | q | \sqrt{q} | λ_1 | λ_2 |
|-------|-------|--------------|-------------|--------|--------|------------|-------------|-------------|
| 47.9 | 561.6 | 11.72 | 6582 | 0.8720 | 0.6427 | 0.8017 | 1.177 | 1.044 |
| 63.0 | 516.2 | 8.194 | 4230 | | | | | |

from which follows:

$$\begin{aligned}
 w &= \frac{7}{8} \times 1,177 \times 516,2 (0,01638 + \\
 &\quad + \frac{1}{6} 1,044 \cdot 0,1280 \{0,1983 - \frac{1}{4} 1,177 \cdot 0,1280 \cdot 1,6427\}) \\
 &= 2126 (0,01638 + 0,02227 \{0,1983 - 0,0619\}) \\
 &= 2126 (0,01638 + 0,00304) = 2126 \times 0,01942 = \mathbf{41,3} \text{ gr. cal.}
 \end{aligned}$$

But +120 is found (YOUNG). [WINKELMANN (1872) gives -110]. The term with Δv is here 19% of the principal term. We calculate for $\Delta v/v$:

$$\Delta v/v = \frac{1}{24} \times 1,117 \times 0,1280 \times 0,1364 = \mathbf{0,00086}.$$

YOUNG found 0, and GUTHRIE + (1884).

In the expression $\Delta v = (\Delta v)_{norm} + \frac{1}{2} (\beta_2 - \beta_2^0) \Delta_2$ (cf. (8) in § 6) Δ_2 , i. e. the volume contraction on transition of 1 double molecule C_2H_5OH to two single molecules, seems therefore to have a small negative value. But in $w = w_{norm} + Q = w_n + \frac{1}{2} (\beta_2 - \beta_2^0) Q_2 = w_n + \frac{1}{2} (\beta_2 - \beta_2^0) \left(q_2 + \frac{a_2}{(v_2)_{\beta_2^0} (v_2)_{\beta_2}} \Delta_2 \right)$ (cf. e.g. 1_{ass}^a in § 6) Q_2 should also be negative then (leaving q_2 out of account). In reality $\frac{1}{2} (\beta_2 - \beta_2^0) Q_2$ seems, however, to be about 80 gr. cal., which would point to a comparatively large positive value of Q_2 (hence also to a positive value of Δ_2), but seeing the deviating value of WINKELMANN, little can be said with certainty about this. Indeed, we know little or nothing about the value of $\beta - \beta_0$.

5. $C_2H_5OH - CH_3OH$. Here we have:

| p_k | T_k | θb_k | $T_k \cdot id.$ | τ | φ | $\sqrt{\varphi}$ | λ_1 | λ_2 |
|-------|-------|--------------|-----------------|--------|-----------|------------------|-------------|-------------|
| 63.0 | 516.2 | 8.194 | 4230 | 0.8959 | 0.7929 | 0.8904 | 1.113 | 1.003 |
| 78.5 | 513.1 | 6.536 | 3354 | | | | | |

This gives:

$$\begin{aligned}
 w &= \frac{7}{8} \times 1,113 \times 513,1 (0,01084 + \\
 &\quad + \frac{1}{6} 1,003 \cdot 0,1041 \{0,1095^5 - \frac{1}{4} 1,113 \cdot 0,1041 \cdot 1,7929\}) \\
 &= 1999 (0,01084 + 0,01740 \{0,1095^5 - 0,0519^3\}) \\
 &= 1999 (0,01084 + 0,00100) = 1999 \times 0,01184 = \mathbf{23,7} \text{ gr. cal.}
 \end{aligned}$$

The term with Δv would, therefore, in any case be about 9% of the principal term. Further:

$$\Delta v/v = \frac{1}{4} 1,113 \cdot 0,1041 \cdot 0,0576^2 = \mathbf{0,00028}.$$

Accordingly more or less these values would have to be found, when the alcohols were *not* associated. In reality, however $\Delta v/v = 0,00004$ is found, which points to a certain volume contraction in both

alcohols. BOSE¹⁾ found about 0,8 for w at $17^{\circ},3$. This is considerably less than 23,7, so that actually heat is liberated in consequence of the volume contraction.

If *water* is one of the components, the values of Δv and w are generally much greater. Thus e.g. BOSE²⁾ (w) and YOUNG (Δv) found:

| | | |
|---|------------|-----------------------|
| a) $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ | $w = -196$ | $\Delta v/v = -0,030$ |
| b) $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$ | -114 | $-0,026$ |
| c) $\text{C}_3\text{H}_7\text{OH}-\text{H}_2\text{O}$ | $+6$ | $-0,030$ |

To form again an idea of what actually takes place I have once more calculated the quantities w and Δv according to (10^a) and (11) — which formula is, strictly speaking, only valid for normal components, but can yet in approximation be also applied for the calculation of the *normal* effect also in anomalous components. I have done so for

6 $\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}$. We have then:

| p_k | T_k | θb_k | $T_k \cdot id.$ | τ | q | V/q | λ_1 | λ_2 |
|-------|-------|--------------|-----------------|--------|--------|--------|-------------|-------------|
| 63.0 | 516.2 | 8.194 | 4230 | 0.5382 | 0.4551 | 0.6746 | 1.467 | 0.8989 |
| 217.5 | 647.1 | 2.975 | 1925 | | | | | |

From this is calculated:

$$\begin{aligned}
 w &= \frac{1}{2} \times 1,467 \times 647,1 (0,2153 + \\
 &\quad + \frac{1}{6} \cdot 0,8989 \cdot 0,4618 \{0,3254 - \frac{1}{4} \cdot 1,467 \cdot 0,4618 \cdot 1,4551\}) \\
 &= 3323 (0,2153 + 0,06919 \{0,3254 - 0,2464\}) \\
 &= 3323 (0,2153 + 0,0055) = 3323 \times 0,2208 = \mathbf{734} \text{ gr. cal.}
 \end{aligned}$$

For $\Delta v/v$ would be found:

$$\Delta v/v = \frac{1}{4} \cdot 1,467 \cdot 0,4618 \cdot 0,0790 = \mathbf{0,00223}.$$

And thus $+734$ is reduced to -114 , and $+0,0022$ to $-0,0026$. The great volume contraction (for the greater part owing to the water) certainly chiefly determines the strong liberated heat-effect.

We shall not enter further into this, and only briefly return to

¹⁾ At 21° $0,007 \times \frac{1}{2}(32 + 46) = 0,3$, which reduced to $17^{\circ},3$ gives 0,8 (see the tables of L. u. B.).

²⁾ 50 mol. % = 64 weight % gives at a) $-7,77 \times \frac{1}{2}(18 + 32) = -194$ ($19^{\circ},7$) or -196 at $17^{\circ},3$. Further at 72 weight. % of b) $w = -3,55 \times \frac{1}{2}(18 + 46) = -114$ ($17^{\circ},3$). WINKELMANN found the same thing in 1907. And at 77 weight % of c) is $w = +0,50 \times \frac{1}{2}(18 + 60) = +19,5$ (21°) or $+6$ at $17^{\circ},3$.

the question, why the values of a/v^2 will not differ much in many cases, as KATZ thinks he has observed.

10. Some remarks on the values of a/v^2 .

In the first place it may be stated that in $w = \Delta P + a/v^2 \Delta v$, ΔP is, of course, only negligible when in consequence of great volume contraction in associating components (chiefly water) the term with $a/v^2 \Delta v$ greatly preponderates. Only then $w/\Delta v$ may, of course, be put $= a/v^2$ in approximation.

But in the second place $a/v^2 = a/b^2$ is not yet always constant within narrow limits. A look at a table¹⁾ of critical pressures is enough to convince one of this. In water $p_c = 217,5$ atm.; in many elements (metals e.g.) still much higher. In many "ordinary" substances, however, especially organic ones, the critical pressures will be about between 30 and 60 atm., as extreme values. And in many only between 40 and 50 atm.

All this is the consequence of the fundamental *atomistic* values of \sqrt{a} and b , from which the values of \sqrt{a} and b for the molecule can be calculated additively in all compounds according to fixed rules (see my papers on this subject already cited in I).

As an example let us take the following principal elements, of which organic substances are built up.

| | H | C | N | P | O | S | F | Cl | Br | I |
|---------------------|--------|---------|--------|-----|--------|-----|-----|-----|-----|-----|
| $10^5 b =$ | 34(14) | 100(75) | 60(85) | 140 | 70(50) | 125 | 55 | 110 | 165 | 220 |
| $10^2 \sqrt{a} =$ | 1.6 | 3.1 | 2.9 | 6.4 | 2.8 | 6.3 | 2.8 | 5.4 | 6.9 | 9 |
| $10^3 b/\sqrt{a} =$ | 21(9) | 32(24) | 21 | 22 | 25(18) | 20 | 20 | 20 | 24 | 24 |

And as the values of b/\sqrt{a} do not differ so very much, this will, of course, not be the case either for the compounds built up of these elements, since — as was already mentioned — the values of b and \sqrt{a} can be additively calculated from the fundamental values recorded above.

Before concluding I will just draw attention in this connection to the fundamental values of \sqrt{a} in *carbon*. In four single bonds the C-atom is towards the outside quite shaded as regards its attract-

¹⁾ Cf. e.g. p. 7 of my first Paper on the additivity of b and \sqrt{a} in the J. d. Ch. ph. (1916) or These Proc. Vol. XVIII No. 8 p. 1220 et seq.

ive action, by the surrounding atoms or atom groups (Examples CH_4 , CCl_4 , C_2H_6 , CH_3Cl , CHCl_3 , etc., etc. — cf. also p. 22 J. d. Ch. ph.; also SnCl_4 , GeCl_4 , etc.).

In *double bonds*, on the contrary, *part* of the C-atom are left free again, and is $10^2 \sqrt{a} = 1,55$, exactly half¹⁾ of the normal value 3,1. In triple bonds the *whole* C-atom can exert an attractive action towards the outside, so that then $10^2 \sqrt{a} = 3,1$.

Accordingly in the compound under consideration the value of $10^2 \sqrt{a}$ is 1,55 greater for *every* C-atom with double bond, than corresponding single bond. The *amount of energy e*, which contains the term $-\frac{a}{v}$, will, therefore, be *smaller* by a proportional value. WIBAUT (Ch. Weekblad N°. 24 of 17th June 1922, p. 259) really states that the value of the energy of a double bond is from 10 to 20 cal. smaller than in a single bond. All this finds its explanation in the theory concerning \sqrt{a} and b for all possible kinds of compounds given by me in 1916, which theory has, unfortunately, remained unnoticed by many up to now.

Tavel sur Clarens (Suisse), Sept.—Oct. 1912.

¹⁾ Thus e. g. in all aromatic compounds, in C_6H_6 etc.; compare the table on p. 20 J. de Ch. ph.

Physics. — “On WHITTAKER’s *Quantum mechanism in the atom*”.
By Prof. H. A. LORENTZ.

(Communicated at the meeting of October 28, 1922).

§ 1. Some months ago WHITTAKER¹⁾ has proposed an interesting model by means of which the quantum properties of the atom can be accounted for to a certain extent, the model showing in the first place how it may be that, in the collision of an electron against an atom, the former loses either no energy at all, or just a definite amount of it. In what follows I shall offer some remarks about the action between an atom and an electron, as it would be according to WHITTAKER’s views.

WHITTAKER supposes that, when an electron approaches an atom, a “magnetic current” is set up in this particle, comparable with the electric current that is excited in a diamagnetic particle by the approach of a magnetic pole. In this latter case the induced current makes the particle repel the pole (LENZ’s law) and similarly in the former case the magnetic current gives rise to a force tending to stop the motion of the electron.

The theory takes the simplest form when it is assumed that there are not only “electric charges”, but also “magnetic” ones, accumulations of positive or negative magnetism. By the introduction of these into the fundamental equations, the parallelism between the electric and the magnetic quantities can be clearly brought out.

§ 2. Let ρ be the density of the electric charge, \mathbf{v} the velocity of one of its points, and similarly μ the density of magnetic charge, \mathbf{w} its velocity; further \mathbf{d} the electric force or the dielectric displacement in the aether, and \mathbf{h} the magnetic force or magnetic induction. Then we have the fundamental equations

$$\operatorname{div} \mathbf{d} = \rho, \quad (1)$$

$$\operatorname{div} \mathbf{h} = \mu, \quad (2)$$

$$\operatorname{rot} \mathbf{h} = \frac{1}{c} (\dot{\mathbf{d}} + \rho \mathbf{v}), \quad (3)$$

$$\operatorname{rot} \mathbf{d} = -\frac{1}{c} (\dot{\mathbf{h}} + \mu \mathbf{w}) \quad (4)$$

¹⁾ E. T. WHITTAKER, On the quantum mechanism in the atom, Proc. Royal Society Edinburgh **42** (1922), p. 129.

The force with which the field acts on unit of electric charge is given by

$$\mathbf{f} = \mathbf{d} + \frac{1}{c} [\mathbf{v} \cdot \mathbf{h}] \dots \dots \dots (5)$$

and there is a corresponding force

$$\mathbf{g} = \mathbf{h} - \frac{1}{c} [\mathbf{w} \cdot \mathbf{d}] \dots \dots \dots (6)$$

acting on unit of magnetic charge.

Remarks on the fundamental equations.

1. In order to simplify the mathematical treatment all quantities occurring in the equations are considered as continuous functions of the coordinates.

2. We shall suppose that, while points of an element of volume move with the velocity \mathbf{v} varying from point to point, the electric charge of the element remains constant, so that the density ρ changes in the inverse ratio as the size of the element. We shall make a similar assumption concerning the magnetic charge. By these assumptions the distributions, both of the electric current $\mathbf{d} + \rho \mathbf{v}$ and of the magnetic current $\mathbf{h} + \mu \mathbf{w}$ are made to be solenoidal, as they must be if equations (3) and (4) shall be true.

3. For the sake of generality we have introduced different symbols \mathbf{v} and \mathbf{w} for the velocities of the electric and the magnetic charges. These charges may be imagined as penetrating each other and having independent motions.

§ 3. The fundamental equations form a consistent system and are in good agreement with ideas and theorems which physicists would be very unwilling to give up.

The force acting on the electric and the magnetic charges contained in an element of volume, taken per unit of volume, is given by

$$\rho \mathbf{f} + \mu \mathbf{g} = \rho \mathbf{d} + \mu \mathbf{h} + \frac{1}{c} [\rho \mathbf{v} \cdot \mathbf{h}] - \frac{1}{c} [\mu \mathbf{w} \cdot \mathbf{d}]$$

and for the x -component of this force one finds after some transformations

$$\rho f_x + \mu g_x = \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} - \frac{\partial G_x}{\partial t}$$

where

$$\begin{aligned}
 X_x &= \frac{1}{2} (d_x^2 - d_y^2 - d_z^2) + \frac{1}{2} (h_x^2 - h_y^2 - h_z^2), \\
 X_y &= d_x d_y + h_x h_y, \quad X_z = d_x d_z + h_x h_z, \text{ etc.}, \\
 \mathbf{G} &= \frac{1}{c} [\mathbf{d} \cdot \mathbf{h}].
 \end{aligned}$$

This shows that the ponderomotive forces can still be expressed by means of MAXWELL'S stresses and of the electromagnetic momentum \mathbf{G} . It should be noticed that this is possible because we have the positive sign in (5) and the negative sign in (6).

The well known expressions for the electric and the magnetic energy and for the flow of energy likewise remain unchanged. Indeed, starting from the fundamental equations, one finds for the work, per unit of time and unit of volume, of the forces exerted by the field

$$\begin{aligned}
 (\rho \mathbf{f} \cdot \mathbf{v}) + (\mu \mathbf{g} \cdot \mathbf{w}) &= - \frac{\partial E}{\partial t} - \text{div } \mathbf{S}, \\
 E &= \frac{1}{2} (\mathbf{d}^2 + \mathbf{h}^2), \quad \mathbf{S} = c [\mathbf{d} \cdot \mathbf{h}].
 \end{aligned}$$

§ 4. If the distribution and the motion of the charges are known, the field can be calculated by means of two scalar potentials φ, χ and two vector potentials \mathbf{a}, \mathbf{b} . These functions are given by the formulae

$$\begin{aligned}
 \varphi &= \frac{1}{4\pi} \int \frac{[\rho]}{r} dS, & \chi &= \frac{1}{4\pi} \int \frac{[\mu]}{r} dS, \\
 \mathbf{a} &= \frac{1}{4\pi c} \int \frac{[\rho \mathbf{v}]}{r} dS, & \mathbf{b} &= \frac{1}{4\pi c} \int \frac{[\mu \mathbf{w}]}{r} dS,
 \end{aligned}$$

in which the integrations have to be extended over all space. The distance from the point for which one wants to determine the potentials for the time t is denoted by r and the meaning of the square brackets is that the quantities ρ , etc. have to be taken such as they are at the time $t - \frac{r}{c}$.

In terms of the potentials we have for the field

$$\begin{aligned}
 \mathbf{d} &= - \frac{1}{c} \dot{\mathbf{a}} - \text{grad } \varphi - \text{rot } \mathbf{b}, \\
 \mathbf{h} &= - \frac{1}{c} \dot{\mathbf{b}} - \text{grad } \chi + \text{rot } \mathbf{a}.
 \end{aligned}$$

§ 5. We shall now suppose, following WHITTAKER, that in the atom there is a circular ring R , over which magnetism is uniformly distributed. We shall consider it as very thin, so that we may speak

of a "line", and we shall denote by a the radius and by k the amount of magnetism per unit of length. Let the centre O be taken as origin of coordinates, the axes OY and OZ being in the plane of the circle, and let s be the distance from a fixed point, measured along the circle. The positive direction of s will be determined by the rotation $OY \rightarrow OZ$, and will therefore correspond, as we shall say, to the direction of OX . We shall finally suppose the ring to be a rigid body that can only rotate about OX , and we shall in the first place calculate the couple acting on it when an electron with charge e moves in the neighbourhood.

The force on an element ds is $k\mathbf{g}ds$ and its moment with respect to OX $a k \mathbf{g}_s ds = a k \mathbf{h}_s ds$. Thus the resultant couple is $a k \int \mathbf{h}_s ds$, where the value of the integral may be deduced from (3). For this purpose we imagine some stationary surface σ having the circle R for its boundary and the normal n to which is drawn in a direction corresponding to the positive direction of s . Then, if this surface does not intersect the electron,

$$\int \mathbf{h}_s ds = \frac{1}{c} \int \mathbf{d}_n d\sigma = \frac{1}{c} \frac{d}{dt} \int \mathbf{d}_n d\sigma \dots \dots (7)$$

We shall suppose the motion of the electron to be so slow and to change so slowly that it may be said, in any of its positions P , to be surrounded by the electric field that would exist if the electron were at rest in that position. Then the last integral in (7) has the value $\frac{e}{4\pi} \omega$, if ω is the solid angle subtended at P by the ring R , the sign of ω depending on the direction, towards the positive or the negative side, in which straight lines drawn from P pass through the surface. Hence, the equation of motion of the ring will be (ϑ angular velocity, Q moment of inertia)

$$Q \frac{d\vartheta}{dt} = \frac{ake}{4\pi c} \frac{d\omega}{dt} \dots \dots (8)$$

If this equation is to hold for a certain lapse of time, the surface σ must be chosen in such a way as not to be traversed by the electron during that interval.

Now, two cases must be distinguished, the electron passing or not passing across the circular plane within the ring, or, as we shall say, through the ring. In the latter case, σ may be made to coincide with the circular plane and we shall have, both before and after the encounter, if the electron is at a great distance,

$\omega = 0$. In the former case this will not be true. Let us suppose that the electron goes through the ring once, in the positive direction, and let A and B be two positions, before and after the encounter, both far away from the ring. Then, whatever be these positions, provided only that they do not coincide, we can choose the surface σ in such a way that it is not intersected by the path of the particle from A to B , and that $\omega = 0$ at the point A . It is easily seen that then the final value will be $\omega = 4\pi$.

By integration of (8) one finds

$$\vartheta = \vartheta_0 + \frac{ake}{4\pi c Q} \omega, \dots \dots \dots (9)$$

if ϑ_0 is the angular velocity which the ring may have had before the encounter.

§ 6. We have next to consider the motion of the electron. The rotation of the ring constitutes a magnetic current

$$i = ak\vartheta \dots \dots \dots (10)$$

giving rise to an electric field that is easily determined if we suppose it not to differ appreciably from the field that would exist if i were constant. The calculation, exactly similar to that of the magnetic field due to an electric current (the vector potential \mathbf{b} is first determined and then $\mathbf{d} = -\text{rot } \mathbf{b}$) leads to the result

$$d_x = -\frac{i}{4\pi c} \frac{\partial \omega}{\partial x}, \quad d_y = -\frac{i}{4\pi c} \frac{\partial \omega}{\partial y}, \quad d_z = -\frac{i}{4\pi c} \frac{\partial \omega}{\partial z}, \dots (11)$$

from which, combined with (10) and (9), we can deduce that the force $e\mathbf{d}$ acting on the electron depends on a potential

$$\psi = \frac{ake}{4\pi c} \vartheta_0 \omega + \frac{a^2 k^2 e^2}{32 \pi^2 c^2 Q} \omega^2 \dots \dots \dots (12)$$

If we wanted exactly to determine the motion we should also have to take into account the force with which, owing to its velocity, the electron is acted on by the magnetic field that is due to the ring and to stationary magnetic charges eventually existing in the atom, and so the problem would become very difficult. Since, however, the latter force does no work, we can write down the equation of energy

$$\frac{1}{2} m v^2 = \frac{1}{2} m v_0^2 - \psi, \dots \dots \dots (13)$$

(v_0 the initial velocity at a point where $\omega = 0$) and this is sufficient for some interesting conclusions.

Indeed, if the electron has not passed through the ring, we shall have finally $\omega = 0$, $\psi = 0$, so that at the end of the encounter the angular velocity of the ring and the velocity of the electron will again have their initial values ϑ_0 , v_0 . This will also be the case if the electron goes twice through the ring, first in the positive and then in the negative direction.

If, however, it goes through the ring no more than once, the final value of ω will be 4π and according to (12) and (13) the electron will have lost an amount of energy

$$\frac{a k e}{c} \vartheta_0 + \frac{a^2 k^2 e^2}{2 c^2 Q}$$

The ring will have gained just as much. This follows directly from (9) and also from the remark that, as may be seen by (9) and (13),

$$\frac{1}{2} m v^2 + \frac{1}{2} Q \vartheta^2$$

remains constant during the motion.

In the case $\vartheta_0 = 0$ the energy that is imparted to the ring by an "effective" encounter is given by

$$\frac{a^2 k^2 e^2}{2 c^2 Q} \dots \dots \dots (14)$$

This agrees with WHITTAKER'S result. In his calculations he has confined himself to a motion of the electron along the axis of the ring, but the preceding considerations show that the theory can easily be generalized. However, it is also seen that, if in an effective encounter the ring is to receive the amount of energy represented by (14), the rotation which may have been imparted to it by a previous encounter, must first have disappeared in one way or another.

§ 7. If, in the case $\vartheta_0 = 0$, the electron is to pass through the ring for good and all, it must initially have at least the amount of energy (14). If it has less, it can by no means get beyond a point, where

$$\psi = \frac{1}{2} m v_0^2, \quad \omega = \frac{4\pi c v_0}{a k e} \sqrt{m Q} \dots \dots \dots (15)$$

Such a point is really reached, the electron returning after having got to it, when the motion is along the axis. In general, however, the problem is less simple. The locus of the points which satisfy the condition (15) is a surface limited by the circle R and having, for a somewhat high value of v_0 , the shape of a wide bag lying on the positive side of the circle, which forms its opening. An

electron that flies into this bag can never leave it across the surface which it will perhaps not reach at all. Indeed, it may be that, before the velocity is exhausted, its direction comes to be tangential to a surface $\omega = \text{const.}$, characterized by a value of ω smaller than the one given by (15). It seems probable that in such a case the electron, after having moved in the bag for a certain length of time, will leave it through the opening, but it is difficult to make sure of this.¹⁾

§ 8. In WHITTAKER'S model the ring R is made up of the poles, of equal signs, of a number of magnets arranged along radii of the circle and having their opposite poles at or near the centre. It might seem at first sight that in a structure of this kind the magnets can be replaced by perfectly conducting solenoids carrying pre-existent electric currents, so that we can do without magnetic charges.

In reality, however, no satisfactory model can be obtained in this way. This is seen most easily when the electron is supposed to move along the axis OX . In the magnetic field due to this motion the lines of force are circles around the axis, and therefore the force acting on an element of current at a point P , is directed along a line lying in the plane POX . For such a force the moment with respect to OX is zero; consequently, neither a solenoid nor a system of solenoids can be acted on by a couple tending to produce a rotation about OX .

Thus it would seem that the hypothesis of "magnetism" existing independently of electric currents is quite essential in WHITTAKER'S model. I need not speak at length of the reasons for which such an assumption is not to be readily admitted. Let it be remarked only that the equations (1)—(6), though forming a consistent system, do not allow us to establish variation theorems of the kind of HAMILTON'S principle. In this principle we are concerned with the *difference* between the potential and the kinetic energy, so that, in the equations, the two energies do not occur in the same way. Now, if there are only electric charges, we can, as is well known, arrive at an equation of the Hamiltonian form, in which $\frac{1}{2}d^2$ takes the place of the potential and $\frac{1}{2}h^2$ that of the kinetic energy. If there are only magnetic charges, there is a similar formula, in which, however, the electric

¹⁾ An interesting discussion of this question has been given (Phil. Mag. 44, 1922, p. 777) by Mr. B. B. BAKER, who has considered the case of an electron not moving along the axis of the ring, without, however, taking into account the forces that may arise from the existence of a magnetic field.

and the magnetic energy have changed their parts. It is clear that it must be difficult to combine the two theorems into one.

I must not omit to say that WHITTAKER does not want to attach too great importance to the special form of his model. He aptly remarks that, after having obtained a satisfactory system of equations, we may discard the model by which we have been led to it. What is especially interesting in WHITTAKER's idea seems to me to be this, that it shows the possibility of a sharp criterion by means of which it can be decided whether an encounter is effective or otherwise. Such a criterion there must certainly be.

§ 9. Generalization of the model. Suppose that there is in the atom a definite closed circuit s , in which a magnetic current i may circulate, the energy being $\frac{1}{2} Li^2$. Then we have the differential equation

$$L \frac{di}{dt} = \int \mathbf{h}_s ds,$$

or, if an electron moves near the atom,

$$L \frac{di}{dt} = \frac{e d\omega}{4\pi c dt}.$$

Take this instead of (8), and combine it with (11). The amount of energy that is transmitted in an effective encounter (initially $i=0$) is now found to be

$$\frac{e^2}{2c^2 L} \cdot \dots \dots \dots (16)$$

In order to obtain a "vibrator"¹⁾ we can link the circuit s with another circuit s' , in which an electric current can circulate (no resistance, energy $\frac{1}{2} L' i'^2$); indeed, we have

$$L \frac{di}{dt} = \frac{1}{c} i' \quad , \quad L' \frac{di'}{dt} = -\frac{1}{c} i.$$

The frequency is given by

$$v = \frac{1}{2\pi c \sqrt{LL'}}.$$

If now an electron passes through the circuit s in a time that is short in comparison with the period, the vibrator receives the amount of energy (16) and this amount will subsequently be radiated. It will be equal to $h\nu$ if

$$\frac{\pi e^2}{c} \sqrt{\frac{L'}{L}} = h.$$

¹⁾ Cf. WHITTAKER, l.c. § 5, p. 139.

One can also try to illustrate other phenomena by means of the model. In its passage from one stationary state of motion to another an electron may be imagined to go through the circuits of a vibrator, so that the energy which it loses is first imparted to the vibrator and then radiated by it. Conversely, after having taken in some way from a beam of incident light the energy $h\nu$, the vibrator could give this energy to an electron that passes through it at the right moment. But in all this we are confronted with very serious difficulties.

Psychiatry. — *“Concordance of the Laws of some Psychological and Physiological Phenomena”*. By Prof. E. D. WIERSMA.

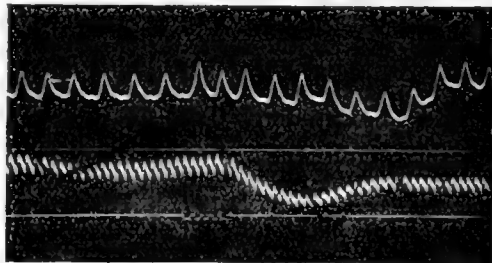
(Communicated at the meeting of September 30, 1922).

The phenomena of consciousness are attended with material changes in the brain. There is an uninterrupted continuity in the anatomic as well as in the psychic phenomena. The two groups of phenomena run parallel. A change in the one will be accompanied by a change in the other. Whether we consider the phenomena of consciousness from the psychological or the physiological standpoint, in both cases the result will be the same, because the changes in the one differ from those in the other not intrinsically but only in form. Memory, which we conceive to be the retention and reproduction of previous impressions, has been considered physiologically and psychologically. First ARISTOTLE and afterwards HERING have looked upon it as a general function of the organised matter. SEMON, who has written a pre-eminent monograph on the Mneme, deemed the ordinary terminology inadequate, as it concerned chiefly the phenomena of consciousness. He, therefore, introduces other terms, as engrams, i.e. the organic changes evoked by a stimulus; the retention of those impressions, which afterwards may again come to us as consciousnesses, is the mneme; and the stimuli by which the action of the primary stimulus can be re-aroused, are termed ekphoric stimuli. Under certain conditions permanent connections are formed between the several engrams, which have been termed “regular tracks”. By the side of this anatomical interpretation the psychological explanation may be put forward. We know for certain that every impression leaves an after-effect in consciousness. Mental tests on secondary function, psycho-analysis, the symptoms of hysteria, hypnosis have conclusively established the existence of these after-effects. That these after-effects may become consciousnesses again through association, is borne out by self-observation and by experiment. Thus the psychological conception may be formed directly, whereas for the physiological we have first to pre-suppose all sorts of organic changes, for we are still completely ignorant of the real existence of the organic engrams and the regular tracks. In strictness this

interpretation is physiological only on the outside; at bottom it is psychological.

Emotions reveal themselves in two ways: Self-observation tells us what emotion in reality is, and from the expression of emotions we deduce what the feelings of the affected individual really are. We know that these peripheral phenomena play so important a rôle that some regard the expression of an emotion in reality as the source of emotion, as a conscious progress. Many psychologists still adhere to this "JAMES-LANGE-theory". However, LEHMANN has shown by dint of many arguments that emotion is primary and expressional movement is secondary. One of his arguments is that the change in the blood-supply, in respiration etc., is posterior to the real emotion. The experiment upon which this argument is based, is open to objection, as it is often difficult to make out where exactly the change in the plethysmogram or the breathing begins. This induced me to repeat the experiment registering at the same time the psychogalvanic reaction. In comparing the plethysmogram with the psycho-galvanogram the latter appears to be more reliable, as is borne out by the subjoined curves.

Respiration
Galvanogram
Plethysmogram



The beginning of the reaction is clearly marked, whereas in the plethysmogram it is often doubtful with which pulsebeat the reaction really begins. The subjoined table also clearly indicates that the

Physiological reactiontimes to pain-sensations
in $\frac{1}{100}$ sec.

| Galvanogram | Plethysmogram |
|-------------|---------------|
| 220 | 335 |
| 230 | 360 |
| 210 | 280 |
| 210 | 350 |

reaction-times of the psycho-galvanogram are shorter and much more constant.

These physiological reactions times, of which I mention only a few, are considerably longer than the psychological reaction times to pain-stimuli which occur directly after the touch-stimuli.

Thus, although emotion i.e. the psychical, is to be considered as primary, it is nevertheless a fact that the expressional movements largely influence the nature and the intensity of emotion. Intense emotions become less vivid through strong expressional movements.

Having a good cry and screaming lessens our grief, hysteric affective conditions, which accompany weeping and screaming are of short duration, the raptus melancholicus has soon spent itself. Here we have to do with an inhibitory process of two co-existing complexes of consciousness. The experience of the violent expressional movements inhibits the emotion.

This accounts for the custom among some uncivilised peoples of dissipating grief by selfmutilation. Not only involuntary but also voluntary expressional movements inhibit emotion. The intensity of a sad mood is often lessened by assuming the attitude and the countenance of cheerfulness.

So far we have seen that conscious as well as unconscious will-acts bear upon emotion in the same way. Conversely, we will now discuss the way in which emotion affects the will-acts.

Emotions exert a great influence upon other complexes of consciousness. They largely inhibit them, because attention clings to them tenaciously. Regular thinking is impossible. Voluntary movements are also inhibited. We don't get on with our work, all our activities slacken, and in pathological cases, such as melancholy, a complete relapse may ultimately set in. Again, this does not apply to voluntary movements only. Also the unconscious efferent impulses are subject to the same influence. CANNON¹⁾ showed that in cats, in a state of emotion, the food remained in the stomach longer than in that of normal cats. Similar inhibitory processes occur in man. A melancholiac secretes less saliva and fewer tears. This can be established experimentally.

Furthermore a distinct decrease of motility of the stomach and the intestine is demonstrable in man. When administering 0,1 l. K. in the empty stomach according to SAHLI's²⁾ prescription, iodine will be found in the urine and in the saliva under normal conditions after 15 minutes. According to SAHLI I. K. is not resorbed

¹⁾ CANNON: Bodily Changes in Pain, Hunger, Fear and Rage. 1918.

²⁾ SAHLI: Klinische Untersuchungsmethoden I, p. 564 u. p. 568.

at all in the stomach, or only after a long interval, so that with a decreased motility of the stomach the I-reaction in urine and saliva will appear later than in normal cases. This experiment was performed with some melancholias and with some normal persons:

| Iodine-reaction in urine | | | | Iodine reaction in saliva | | | |
|--------------------------|----------|--------|---------|---------------------------|--------|--------|---------|
| Melancholy | | Normal | | Melancholy | | Normal | |
| A | 105 min. | K | 15 min. | A | — min. | K | 15 min. |
| B | 105 " | L | 15 " | B | 165 " | L | 45 " |
| C | 90 " | M | 15 " | C | 90 " | M | 15 " |
| D | 60 " | N | 15 " | D | — " | N | 15 " |
| E | 75 " | O | 15 " | E | 90 " | O | 15 " |
| F | 75 " | | | F | 45 " | | |
| G | 45 " | | | G | 90 " | | |
| H | 60 " | | | H | 60 " | | |
| I | 45 " | | | I | 45 " | | |

This table shows distinctly the retardation of the reaction in urine and saliva in cases of melancholy. It is very well possible that this retardation is not due only to the gastric function, but that at the same time a slower resorption has taken place in the intestine and inhibition in the secretion of the kidneys and the salivary glands.

Conclusive evidence regarding the retardation of the movement of the stomach and the intestine can be afforded by Röntgenograms.

In the morning 150 grs of bariumsulphate was administered with 500 grs of porridge in the empty stomach. Normally the stomach will then be quite empty again after 4—6 hours. In the stomach of a melancholiac I found after 4 hours still a very large quantity; after 10 hours a rather large quantum and after 24 hours still distinct traces of the bariumsulphate. After a 10 hours' fast this patient took food again, so that the bariumsulphate, then present, may have been mixed up with the food. The latter registration, therefore, is not quite reliable.

The decreased motility of the intestine also manifests itself distinctly. Under normal conditions all the bariumsulphate is removed from the small intestine after 10 hours. The examination of another

melancholiac proved clearly that after this lapse of time still considerable amounts are present.

In the same way slower motility of the large intestine can also be established. In one patient the food remained in the large intestine for 4 days, in others for more than 5 days.

It is evident that relative to the emotions the conscious will-acts and the unconscious centrifugal impulses are subject to the same rules.

In discussing the reflexes it appeared that mutual inhibition of co-existing phenomena of consciousness also applies to simultaneous unconscious centrifugal impulses. BABINSKI's reflex is superseded by the normal plantar reflex, the sucking- and the gait-reflex by other movements, arising later, the diminution of the patellar reflex is the result of centrifugal impulses that are always present, the tonus of the antagonists diminishes through contraction of the agonists. All this proves that the co-incidence of involuntary efferent impulses gives rise to a mutual inhibition in precisely the same way as with the co-incidence of conscious will-acts. Hereby a complete co-operation of the muscles is rendered possible.

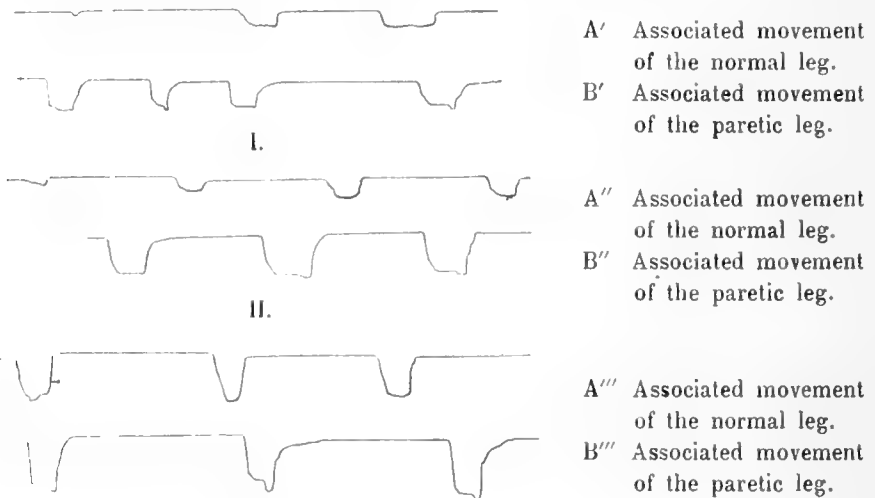
Closely related to this are the associated movements. When a child begins to grasp at things with the right hand, the left one accompanies it. A few years later these "co-operations" disappear. They are inhibited. Whence does this inhibition arise? An incessant flux of impressions passes from the extremities to the area of consciousness, imparting information regarding attitude and position of the limbs, so that the easiest attitude will be selected and every undesired movement will be counteracted. At first this occurs arbitrarily, afterwards involuntarily and reflexly. A gymnast and a skater will first try to counteract the unnecessary movements, afterwards this happens involuntarily. That the inhibitory action is exerted by these simultaneous centrifugal reflex impulses may be gathered from the following facts:

Associated movements are strongest in the first years of life. When the position reflexes begin to develop, the associated movements will gradually cease.

They will recur or intensify in highly emotional situations. The pre-occupation resulting from them will not only eliminate all complexes of the central area of consciousness, but also the subliminal position-reflexes will be affected by them, so that the associated movements of a deeper level will recur. In the same way in con-

ditions of dementia, as with dementia paralytica and dementia senilis, in which a general diminution occurs of the degree of consciousness, the position-reflexes are affected prior to the associated movements. It is obvious, therefore, that the associated movements will recur.

Associated movements manifest themselves most distinctly with an affection of the pyramidal tract, because then the conduction of the centrifugal impulse, which acts inhibitory, is lacking. This is easy to demonstrate in patients with cerebral hemiplegia, because in these cases the associated movement of the paretic leg can be directly compared with the movement of the healthy leg. In my investigation I availed myself of the following associated movement. When a subject, in dorsal position, is instructed to raise the right leg, the left leg will be pressed down, of which fact the experimenter may readily convince himself by putting his hand under the left heel. A distinct pressure will then be perceived, which will increase with a greater effort of the right leg. The associated movement of the left leg may be reinforced by opposing a resistance to the movement of the right leg. The registration of the associated movement happens in the following way. The left leg is suspended in a loop a little way above the heel. The loop is attached to a steel-yard by means of a cord that passes over a pulley. When the leg is pressed down the force of the effort can be read accurately from the steel-yard. To the cord is fastened a stylus, which records the movement directly on a rotating kymograph. In patients with cerebral hemiplegia the associated movement on the paretic side appears to be much more pronounced than on the healthy side. In the subjoined curves A', A'' and A''' represent the associated movements of the normal leg;



B', B'' and B''' those of the paretic leg. In curve I the associated movement is registered without any impediment to the other leg. In curve II the leg is weighted with 1700 grms, and in curve III with 2900 grms.

The annexed table also shows clearly that the associated movement of the normal side is invariably inferior to the one on the paretic side.

| Curve I | | Curve II | | Curve III | |
|------------|-------------|------------|-------------|------------|-------------|
| normal leg | paretic leg | normal leg | paretic leg | normal leg | paretic leg |
| gr. | gr. | gr. | gr. | gr. | gr. |
| 162 | 767 | 225 | 975 | 1247 | 1175 |
| 490 | 767 | 427 | 873 | 1302 | 1201 |
| 438 | 751 | 592 | 876 | 1064 | 1453 |

Associated movements are on a par with the associations of the phenomena of consciousness. As known, the laws under which these associations originate have been reduced to the simultaneous associations. That this is also the case with the associated movements is evident. The child begins to stretch both hands when grasping at something, which evolves a simultaneous association. When, in later years the grasping right hand is accompanied by a movement of the left one, this is in reality an association effected in precisely the same way, in which e.g. the image of a person is called up when hearing his name.

Associations can be facilitated or inhibited. In this also the associated movements bear so close a resemblance to associations, that the two processes must be considered analogous.

Associations are inter alia facilitated by greater intensity of the associated ideas. EBBINGHAUS introduced meaningless syllables to be learned by heart in a certain order. Reproduction in a reversed order was not possible. Of this MÜNSTERBERG has put forward an explanation: In reciting the alphabet, a and b remain for some time in consciousness. In hearing b there is still a faint after-effect of a. Therefore, in hearing a, b will be reproduced sooner than, conversely, a will be reproduced in hearing b. In the associated move-

ments the same phenomenon manifests itself. The intensest associated movements persist longest. They display a much greater resistance to the inhibitor. There are people with whom some associated movements persist through life e.g. the mouth-movements when they are using scissors.

Associations are also promoted by the intensity of the associating idea. Memory-images will be reproduced the more readily according as the associating idea is more intense and distinct. Experience e.g. teaches us that visual, and auditory sensations arouse associations sooner and more distinctly than the vague olfactory, and gustatory sensations. We can observe a similar phenomenon in the associated movements. The curves obtained from the above experiments go to show that, when the movement of the one leg is interfered with by a weight thus inciting the subject to greater exertion, the associated movements of the other leg also increases.

In curve II the weighting of both the paretic, and the normal leg considerably increased the associated movements on either side. When, as in curve III the weight is very heavy, the demand upon the paretic leg is so great, that the ensuing associated movement of the normal leg does not differ much from that of the paretic leg. Curves I and II also demonstrate that, with a series of movements of the paretic leg the associated movements of the normal leg increase in magnitude. This is due to a greater demand upon the paretic leg consequent on fatigue.

The associations of the phenomena of consciousness can also be inhibited. Here again the associated movements exhibit analogous phenomena. As known, the association of the phenomena of consciousness is interfered with by co-existing complexes of consciousness and the degree of the interference depends on their homogeneity. The reproduction of visual ideas is counteracted by other sight-experiences in a higher degree than e.g. by auditory experiences. In forming a visual image of a situation, we shut our eyes. Speaking a foreign language is more difficult than to read it, because the word in our native tongue arouses many associations which act inhibitive, whereas the foreign word awakens no other associations than those called up by the native word. It is just the same with the associated movements. The impulses exciting them, are ousted already by the co-existing efferent impulses of the position reflexes. It is evident, that also here there is an analogy to the inhibition exerted upon sight-associations by other visual impressions, and to the inhibition, exerted by the multitude of associations, upon our efforts to speak a foreign language.

The so-called mediate associations occur, when memory-images flash into consciousness that seem to have no connection with the associating idea. On closer inspection it will appear that the associated idea has not linked itself directly to the associating idea, but to an unconscious memory-image. Without this intermediary the association would not have originated. The strange freaks of normal men, of hystericae and in cases of dementia praecox, may often be assigned to these intermediary ideas unsuspected at the moment of the association. Afterwards they crop up again by concentrating ourselves entirely upon the association, or by other means, such as association experiments, hypnosis, etc. Similar phenomena occur in physiological processes. Many renal diseases are attended with hypertrophy of the heart. The real relation is still a moot point; probably the enlargement of the heart arises from the increase of the blood-pressure, which some believe to result again from the retention of the intermediary products of metabolism, or, according to others, from an excess of adrenalin-products. It is evident, then, that here also we have to do with two phenomena mediately connected. A similar example is afforded by hypertrophy of the uterus in pregnancy. This is not a direct action of the foetus upon the uterus, as this hypertrophy also reveals itself in extra-uterine pregnancy. Now, inquiries have proved that most probably internal secretion of the corpus luteum comes into play here. So, here again we observe a connection between the two phenomena, through the mediation of one that has long remained unsuspected. The hypertrophy of the mammary tissue in pregnancy is assignable to the same cause.

We have already referred to the phenomena of ousting the centrifugal impulses by conscious will-manifestations and even by other reflex-impulses, nearer to the threshold of consciousness. Definite proof of it is afforded by the superseded reflexes, as that of BABINSKI and the sucking reflex, and the superseded associated movements. As stated above, these reflexes have not disappeared; they recur when the inhibitory influences do not exist any more. In this respect they resemble retrograde amnesia. Here also memory images are stamped out by intensely operating, often highly emotional, impressions. The memories closest to the threshold of consciousness, still exerting their after-effect upon the centre of consciousness (which proves them to be still coexistent with the superseding stimulus), are thrown back farthest from the view-point. We may, then, put it in this way that HEYMANS'S ingenious idea is applicable to the superseded reflexes as well as to the superseded thoughts, viz.

that their distance-energy is enlarged and their level-energy has decreased.

It seems to me that there is another resemblance of some significance. Perceptions, as we observed, do not fade out altogether, they leave traces, which will be present in consciousness again through association, but which, of themselves, also possess a tendency, a certain potency to emerge. There is a continual competition among the subconscious tendencies. Their potency varies with various conditions inter alia of novelty, emotionality, fortuitous associations. In ordinary circumstances there is an uninterrupted inhibition exerted by other ideas. When this inhibition is taken away, as is the case in dozing and during sleep, these subconscious ideas may be present in consciousness again. This may be brought about by association, but surely their own energy may also co-operate. This appears from the difference in own energy appropriate to various ideas. For example: a personal name may recall the image of the person, but the latter does not always call up the name. An accident will be reproduced more readily when witnessed than when only read about. That own energy of ideas or perceptions to become central consciousnesses, which energy has been termed by HEYMANS distance-energy, is utilized partly by obviating resistances and, when at the ingress into consciousness some energy is still left, this remainder is spent entirely in repulsing the resisting complexes of consciousness as far as possible into unconsciousness. These conditions occur with the just-mentioned retrograde amnesia, analogous phenomena of which are met with in the repulse of some reflexes by others, which lie still nearer to the threshold of consciousness. But HEYMANS also puts the case that there are hardly any resistances, so that there cannot be any question about a loss of distance-energy through repulse. In such a case that energy will be applied in consciousness as energy of association, of sentiment, of thought and of will. Now, do similar manifestations also arise with subconscious phenomena? As regards some reflex manifestations, we are in a position to select such conditions as are perfectly similar to those required for the phenomena of consciousness, so that when they occur there will be no resistances in their way. In this connection we may take it for granted, that knee-jerks are inhibited by simultaneous centrifugal cerebral impulses. Affections of the pyramidal tract have disturbed the conduction of these impulses, so that the knee-jerks are no longer subject to inhibition. Well then, in these conditions many reflex-associations occur, viz. contraction of the adductors, and also frequently of the m. quadriceps of the other leg.

I annex a few other examples, the number of which may still be enlarged.

It is known that the direction of voluntary thinking and acting is determined by the intentional idea in its after-effect. The bias of the mind arouses the most serviceable thoughts and motives; the others are inhibited. This is the course of every process of thought as well when we are simply designing a travelling plan, as when we are working out the most intricate scientific problem. The same holds also for mental development at large. From our earliest youth upwards there is an unconscious tendency by which the adult mind is developed from the simplest data. Physiologically we observe the same process, by which a single ovum develops into the full-grown body. In either case there is a tendency in the line determined by the result to be attained, i.e. the intentional idea.

True, this result is not present in consciousness, but for the rest it is perfectly similar to the intentional idea in its secondary function, because either of them determines the developing process.

In mental growth the innate tendency dictates a certain trend. Great disparities present themselves, e.g. in the types of observation and in individual character. Interest, which is chiefly innate, plays a prominent rôle in the formation of the types of observation. The visual type e.g. shows an affinity for sight-impressions, while it neglects the auditive-, and the motor impressions. In physical development we distinguish a similar difference in trend. The fertilized ovum cell is omnipotent. In it is hidden the power for development of all tissues. Differentiation of this potency appears after repeated division of the cell. Some cells can supply only epithelium, others only connective tissue, or muscular and bony tissue.

From the facts above stated it appears that there is a far-reaching concordance between the laws of some psychological, and, let me put it cautiously, *some* physiological phenomena. Our results justify us in suspecting that with a fuller knowledge of both groups of phenomena a psychological equivalent may be found for every physiological phenomenon.

Physics. "On the Separation of Gas Mixtures by Diffusion in a Flowing Gas". By Dr. G. HERTZ. (Communicated by Prof. P. EHRENFEST.)

(Communicated at the meeting of November 25, 1922).

As is well known, the differential equation: $\Delta \rho = 0$, in which ρ represents the density of the diffusing gas, is valid for stationary phenomena of diffusion in media at rest. This equation does not contain the constant of diffusion of the diffusing gas at all. If, therefore, the diffusion of a gas mixture is considered, the ratio of the partial pressures of the components of the mixture is constant throughout the space, i.e. unmixing does not occur with such a stationary diffusion phenomenon. This however, is different, as will be shown in what follows, with stationary phenomena of diffusion in a moving medium. As such a moving medium we take a flowing gas. Let the velocity of this gas medium be v , and let it satisfy the condition $\text{div } v = 0$. The constant of diffusion of the diffusing gas under definite circumstances be δ , its density ρ , which for the calculation we shall assume to be small compared with the density of the gas medium. The quantity of the diffusing gas passing through the unit surface in the unit of time hence its current density, is equal to the sum of the diffusion and the convection current; it is:

$$i = -\delta \text{ grad } \rho + \rho v$$

For stationary phenomena $\text{div } i = 0$, so that taking into account that $\text{div } v = 0$, we get the following differential equation for such phenomena:

$$\Delta \rho = \frac{1}{\delta} (v, \text{ grad } \rho)$$

In contrast with the equation $\Delta \rho = 0$ holding for a medium at rest, this equation contains the constant of diffusion δ . Accordingly the distribution of the density in space is here dependent upon the constant of diffusion. If, therefore, a gas mixture is made to diffuse in a stationary medium the ratio of the partial pressures is constant. On the other hand this ratio is variable in a moving medium; and this brings about the possibility to use this phenomenon for the separation of gas mixtures.

In what follows two special cases will be treated, which it has been possible to realize experimentally, and which can be used for the separation of gas mixtures. In both cases a gas medium flowing with a constant velocity v is used, the direction of which will be chosen as direction of the negative x -axis. For this case the differential equation is:

$$\Delta \varrho = -\frac{v}{\delta} \frac{\partial \varrho}{\partial x}$$

When we assume $\varrho = \varrho_0$ for $x = 0$, and $\varrho = 0$ for $x = \infty$, we get as a first example the case of diffusion *against* the gas current. The solution is easily seen to be:

$$\varrho = \varrho_0 e^{-\frac{vx}{\delta}}$$

The density of the gas diffusing against the current decreases, therefore, according to an exponential function, the gradient of which depends on the ratio of the current velocity to the diffusion constant. When now a mixture of two gases whose partial pressures for $x = 0$ are ϱ_0 resp. ϱ'_0 diffuses against the current, the following equation is found for the ratio of their partial pressures as function of the place:

$$\frac{\varrho}{\varrho'} = \frac{\varrho_0}{\varrho'_0} e^{-vx \left(\frac{1}{\delta} - \frac{1}{\delta'} \right)}$$

This distribution agrees in form with the distribution of the partial pressures in the field of gravitation determined by the barometer formula, with the exception only that here the quantity $\frac{v}{\delta}$ takes the place of the specific gravity, and the whole pressure gradient can be brought about at a distance of the order of a millimeter.

If this phenomenon is to be used for the separation of a mixture, the gas present at a certain place, e.g. at $x = l$, must be pumped off. The limiting conditions then become $\varrho = \varrho_0$ for $x = 0$ and $\varrho = 0$ for $x = l$. The solution then becomes:

$$\varrho = C \left(e^{-\frac{vx}{\delta}} - e^{-\frac{vl}{\delta}} \right)$$

in which C is a constant. If, as in practice, $e^{-\frac{vl}{\delta}}$ is small compared with 1, C is approximately equal to ϱ_0 . We thus find for the

1) Compare S. HOLST WEBER, Handelingen van het 17e Nederlandsch Natuur- en Geneeskundig Congres, Leiden 1919.

current density of the diffusing gas, i.e. the quantity which diffuses per unit of time through the unit of crosssection against the current:

$$i = v \rho_0 e^{-\frac{rl}{\delta}}$$

If a mixture of two gases which at $x = 0$ have the densities ρ_0 and ρ'_0 diffuses, the ratio of the quantities of the two gases which diffuse per unit of time against the current is equal to:

$$\frac{i}{i'} = \frac{\rho_0}{\rho'_0} e^{-vl\left(\frac{1}{\delta} - \frac{1}{\delta'}\right)}$$

This quantity represents, therefore, the degree of unmixing reached in such a diffusion process; inversely the product vl is determined by the diffusion constants of the gases that are to be separated, and by the degree of unmixing required. In order to make the efficiency also as large as possible, v should be chosen as large as possible and in accordance with this l small, as follows from the equation of the current density.

The second case, which in practice has been realized, is the following one: let again v be the constant velocity of the flowing gas, and let the direction of the current be that of the negative x -axis. At a certain point in this current we now admit the other gas. This gas will then be carried along with the current, and at the same time be scattered to all sides by diffusion. In this case the distribution of the diffusing gas is found by integration of the differential equation:

$$\Delta \rho = -\frac{v}{\delta} \frac{\partial \rho}{\partial x}$$

with the limiting condition that at infinity the density of the diffusing gas must be zero. When the point where the gas enters the current, is chosen as origin of the system of coordinates, and the radius vector is called r , we find the solution:

$$\rho = \frac{C}{r} e^{-\frac{v}{\delta} \frac{r+x}{2}}$$

in which C is a constant. The factor $\frac{C}{r}$ represents diffusion in the medium at rest, the exponential function which is due to the current, is of the same nature as in the first case; only instead of v we have here $\frac{v+x}{2}$. If, therefore, a gas mixture is introduced into the current, unmixing takes place in this case as well. Further

the same remarks are valid here as in the first case; thus it is also practical here to choose the current velocity great and geometrical dimensions small to render the quantity attained as great as possible.

All these considerations have completely been confirmed by experiment. In order to effect the separation of gas mixtures by diffusion in a flowing gas in practice, it is first of all required that as a medium a gas be chosen that can be easily separated from the diffusing gases. This can be attained in a simple way by using a vapour as medium gas, which can be condensed after having passed the place where the diffusion is brought about. All the experiments made so far, were carried out with water vapour of 15 to 60 cm. pressure. The use of mercury vapour of lower pressure may, possibly, be still more efficient; this will be further investigated.



Fig. 1.

The chief point in the construction of apparatus for carrying out the process described above, is the production of a constant vapour current. When a gas passes over a sufficient distance through a cylindrical tube, a current is obtained with parallel stream lines, but the velocity is not constant; it decreases from the axis towards the walls of the tube, as is represented in

fig. 1. It is, however, possible to get a current of constant velocity, though over a short distance only, when the gas passes through a wide tube with a suddenly decreasing diameter or when the gas escapes from a vessel through a small hole in the wall. When in this way the medium gas flows from a vessel *A* into a vessel *B* fig. 2, and when the gas mixture that is to be separated, is admitted to the vessel *B*, the case of diffusion against the gas current is realized. The velocity of the current can then always be chosen such that only the component of the gas mixture that diffuses more rapidly, diffuses against the current and reaches the vessel *A*, from which it can be pumped off together with part of the medium gas.

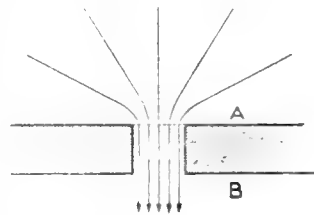


Fig. 2.

This idea was carried out experimentally as follows: the water vapour generated in a vessel heated electrically, flows through *S* (fig. 3) into a tube closed at the bottom by a metal plate *D* of a thickness of 1 m.m. This circular plate of a diameter of 28 m.m. has 30 holes of 1 m.m., each, distributed uniformly over its surface. Through these holes the water vapour enters the vessel *V*, the lower part of which is surrounded by a cooling jacket, so that

the water vapour is condensed. The gas mixture to be separated is admitted through the tube *G*. A part of this mixture diffuses against the current through the holes in *D*; this part can be pumped off with part of the water vapour through the tube *H*. The temperature of the water in the cooling jacket must be regulated in such a way, that the sum of the partial pressure of the water vapour and the pressure of the gas mixture in the vessel *V* is exactly so much smaller than the pressure of the water vapour admitted through the tube, that the required current velocity is obtained. The appliances used to attain this regulation, will be discussed later. The method described has so far been chiefly used to separate helium-neon mixtures, and has proved very satisfactory. Even, when the process of diffusion was executed only once, from such a mixture containing 30% helium, helium could be obtained, the purity of which was so great, that in a Geissler-tube at a pressure of 1 m.m. the neon-lines were not visible with an ordinary spectroscop. Considering the exceedingly great spectral sensitiveness of Helium with regard to very small quantities of Neon, this shows already a very great degree of purity.

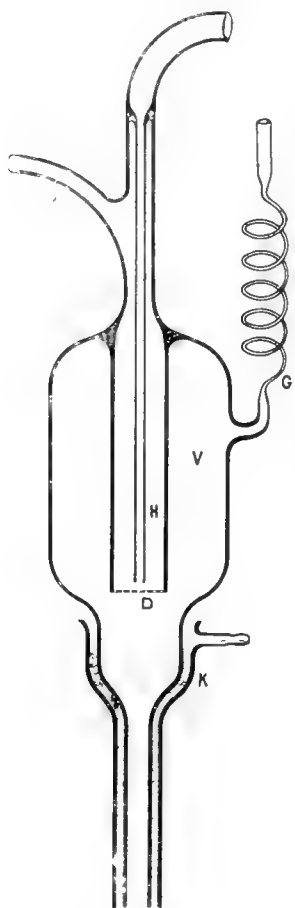


Fig. 3.

Though the unmixing of the gas mixture by diffusion against the gas current was actually as great as was to be expected according to theory, the quantities obtained remained below expectation. This may be explained by considering, that in the method described only part of the cross section of the vapour current is used, because the gas must diffuse from the outside into the jets that issue separately from each hole. In order to deal with greater quantities another apparatus appeared to be more suitable, working according to the second example discussed above. This second case is in so far much more easily realized, as it is not necessary here to keep the current velocity accurately constant. It is immediately seen that with a current as represented in fig. 1, also unmixing of a mixture is to be expected, when this mixture is introduced at a point in the axis of symmetry of the current. The principal part of the

apparatus is reproduced in fig. 4. The water vapour enters through the tube *R*, which is ground off at the end, so that the water vapour leaves the tube in a cylindrical jet. The gas mixture enters through the



tube *G*, ending in a capillary concentric with *R*, the end of which is in a plane with the endplane of *R*. Opposite the tube *R* at a distance of 3 mm. there is a tube *D*, the opening of which is formed by a circular sharp edge of a diameter of 6 mm., and manufactured from metal for the purpose. The outer part of the cylindrical jet coming from *R* is as it were peeled off by the sharp edge. With a suitable choice of the current velocity this outer part of the vapour current practically contains only the component of the mixture which diffuses more rapidly: this component is separated from the water vapour by condensation, and collected in a vessel. By far the greater part of the gas mixture admitted through *G* passes on through the tube *M* with the inner part of the vapour current, is also freed of the water vapour by condensation, and again admitted through *G* by means

of a circulation pump.

If the apparatus is to work well it is chiefly necessary that the velocity of the current is accurately regulated, and besides it is practical to lead the condensed water vapour back; else the water in the heating vessel would diminish too rapidly. Fig. 5 represents the whole apparatus. In the glass vessel *W*, which is 50 cm. long and has a diameter of 10 cm. the water is heated electrically by means of a heating wire wound on a layer of asbestos. The pressure of the water vapour in this space can be determined by means of a thermometer *T* suspended in the vapour. This water-vapour flows through a tube to a bulb *B*, and from there to the tube *R* of the diffusion apparatus, while simultaneously the gas mixture to be separated, enters the tube *G* through a very narrow capillary tube. By the regulation of the pressure of the gas mixture before it enters the capillary tube, an accurate control of the velocity with which the mixture is admitted, is made possible. The two parts, into which the gas current is split up by *D*, pass on through the tubes *H* *M* resp. and reach the condensation vessels *C*₁ and *C*₂, which are provided with cooling jackets *K*₁ and *K*₂. Here the water vapour is condensed, and the water runs back, to *W* as is seen in the figure. The part separated by diffusion is collected in *C*₁, and the rest of the gas mixtures in *C*₂. Both

these parts together with some water-vapour leave the apparatus each through a very narrow capillary. The water vapour is removed by freezing it out. The separated part is received in a vessel, the rest of the gas mixture, however, is again led back to the apparatus by means of a circulation pump.

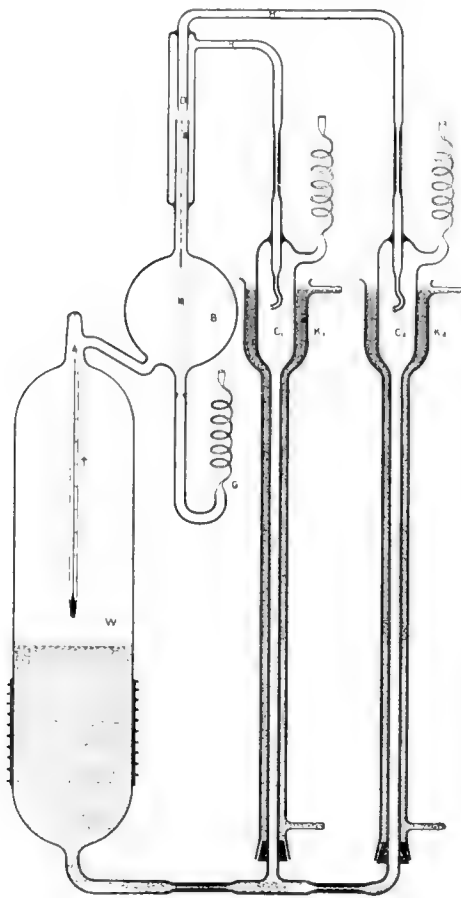


Fig. 5.

The vapour current is controlled by regulating the current in the heating spiral wound on W , and the temperatures in K_1 and K_2 . The latter is effected in such a way that the water flowing through the cooling jackets with accurately constant velocity is beforehand led through a copper tube, surrounded by a heating coil, so that the temperature of the water depends on the current passing through this heating coil. The check on the current velocity is made possible by the capillaries between H and C_1 , and between M and C_2 , these causing a difference of pressure between W and C_1 resp. C_2 , that is in direct ratio to the current velocity in H resp. M . This difference of pressure can be measured by the difference of level between the condensed water in C_1 resp. C_2 and the water in W . Neither the absolute value of the current velocity nor the temperature of the water in K_1 and K_2 need be known; when the level of the water in the two tubes with regard to the level in W is such, that the unmixing of the gas mixture is satisfactory, the heating current need only be regulated so, that this position is maintained.

It is not necessary to keep the temperature, and with it the density of the vapour, accurately constant, for both the current velocity corresponding to a given difference of pressure between the ends of the capillary tube, and the diffusion constants of the diffusing gases are approximately inversely proportional to the density of the

vapour; accordingly the relation $\frac{v}{d}$ characteristic of the diffusion in a flowing gas is not affected by small fluctuations in the vapour density. In order to prevent condensation of the water vapour against the walls, the whole apparatus is enclosed in a box, in which the air is heated a few degrees above the temperature in *W*.

The same degree of the separation is obtained by the first and the second method. As regards the quantity obtained the second method however, is considerably better. Only when it is required to separate small quantities, the former method is preferable, as in the second method a certain minimum quantity is required for the circulation.

It is of importance to consider whether our method of the diffusion in a gas current is more efficient with regard to the separation of isotopes than the methods used up to now. This new method is no doubt superior to the usual way of separation by diffusion. It is, however, possible, that when we apply this method to gases with diffusion-constants differing as little as they do for isotopes, small irregularities in the current may have much greater disturbing influence than in neon-helium mixtures. Nor can it, of course, be expected that a mixture of isotopes should be completely separated by a single process of diffusion, for such a process, supposing it be possible in principle, would require a very long time, as can be calculated from the above given formulae. On the other hand, e.g. in neon, a change in the ratio of mixing of the isotopes of about 30% could be expected as the result of one process of diffusion, so that it might be expected that a fairly far advanced separation can be obtained after not too many repetitions. It is not our intention to use the apparatus described above for the separation of isotopes, as it must undoubtedly be possible to construct apparatus on the same principle, working considerably more rapidly.

Eindhoven, 1922.

*Physical Laboratory of the
"N.V. Philips' Gloeilampenfabrieken."
(Philips' Incandescent Lamp Works).*

Physics. — “*On the Excitation and Ionization Potentials of Neon and Argon*”. (Appendix). By Dr. G. HERTZ. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of November 25, 1922).

In the measurements of the excitation and ionization potentials of neon and argon discussed recently ¹⁾, the value of 20,45 Volts measured by FRANCK and KNIPPING was used as the first excitation potential of helium, in order to determine the absolute value of these potentials. Since then LYMAN ²⁾ succeeded in measuring the spectrum of Helium in the extreme ultra-violet directly. It can be shown from his results, that the values found by FRANCK and KNIPPING for the critical potentials of helium, like HORTON and DAVIES' values, which are in close agreement with them, are too high. As FRANCK ³⁾ shows by a comparison of the values measured optically and electrically, 19.75 Volts must now be taken to be the first excitation potential, which value is accurate within 0.1 Volt. In connection herewith the excitation and ionization potentials of neon and argon, having been measured relatively to helium must also be diminished by 0.7 Volt so that the following values are obtained:

Neon: Excitation potentials: 16.65 and 18.45 Volts.

Ionization potential : 21.5 Volts.

Argon: Excitation potentials: 11.55; 13.0 and 14.0 Volts.

Ionization potential : 15.3 Volts.

The conclusions relating to the optical spectrum are not affected by this correction, as only the potential differences are used for them. Only the term 0.5 s., which corresponds to the normal state of the atom, must be diminished, and becomes 174000 ± 1000 for neon, and 124000 ± 1000 for argon.

Eindhoven.

*Physical Laboratory of the
N. V. Philips' Gloeilampenfabrieken.*

1) These Proc. Vol. XXV N^o. 5 and 6, p. 179.

2) TH. LYMAN, Nature, **110**, 278, 1922.

3) J. FRANCK, Zeitschrift f. Phys. **11**. 155, 1922.

Physics. — “*Further experiments with liquid helium. Q. On the electric resistance of pure metals etc. X. Measurements concerning the electric resistance of thallium in the temperature field of liquid helium.*” (Comm. N^o. 160a from the Physical Laboratory at Leiden). By Prof. H. KAMERLINGH ONNES and W. TUYN.

(Communicated at the meeting of October 28, 1922).

§ 1. *Object of the research. Method of preparing the resistances.*
The place of thallium in the periodic system of elements, between the super-conducting metals mercury and lead, made it seem probable that it would become super-conducting at helium temperatures.

We had at our disposal only rods of thallium from KAHLBAUM¹⁾. From this Mr. P. J. v. D. BAAN, instrumentmaker of the Phys. Lab., extruded wires of 0.2 and 0.5 m.m. thickness; they were bright at first, but quickly became tarnished and grey in colour. At the distance of a few c.m. from the ends of each wire a second short wire was melted on in a small gas-flame; during this process the thallium was protected from oxidation by a layer of melted candle grease. The wire was then wound bifilarly upon a porcelain tube with a double screw thread baked into it, (these tubes were made by the Königliche Porzellan-Manufaktur, Berlin and have been mentioned before in Comm. N^o. 152c § 2) and then the four thallium ends were each soldered to a copper wire, previously attached to the tube. The resistance thus prepared was enclosed in a glass tube made by the chief glass blower of the Phys. Lab. Mr. O. KESSELRING, in the following manner. The ends of this tube through which the copper wires protuded were platinised, coppered, provided with copper caps and sealed up (see also Comm. N^o. 133d, p. 60). To remove the oxidation layer on the *Tl*-wire the resistance was rinsed through the opening at the other end of the glass tube and dried by a moisture absorber and carbon tube; a tap attached

¹⁾ According to a letter from the firm the thallium contained the usual amount of lead; about other impurities nothing was said. The same letter said that the firm did not prepare any “extra” pure material. M. LEVIN (Z.S. f. An. Chem. 45 (1905), p. 31) states that KAHLBAUM-thallium contains 99.91% Tl. N. KURNAKOW, S. ŽEMČUŽNY and V. TARARIN (Z.S. f. An. Chem. 83 (1913), p. 200), only say that they used pure Tl from KAHLBAUM.

to this end of the tube was then closed. By means of a Töpler pump and a suitable arrangement of glass connecting pieces the resistance was then twice rinsed with helium and finally helium to a pressure of 51 c.m. was admitted; after this the glass tube was sealed at the narrow part provided for the purpose. (For the final form see fig. 2 of Comm. N°. 160*b*.) In this way in Dec. 1916 were prepared *Tl-VIII-1916*, diameter 0.2 m.m. with a joint in the bifilar wire, and *Tl-IX-1916*, diameter 0.5 m.m.

§ 2. *Zero determinations.* For determining the zeros, the resistances *Tl-VIII-1916* and *Tl-IX-1916* were placed in glass tubes filled with liquid paraffin (owing to the war conditions no isopentane could be had) or with distilled benzine; the tubes were closed by corks, over which a layer of paraffin was laid. They were placed in ground ice, and the first measurement was made two hours later and repeated with intervals of about half-an-hour. The method of measuring used is either that of overlapping shunts in accordance with KOHLRAUSCH, or that of the compensation of the potential at the terminals of an unknown and a known resistance, connected in series, by means of a compensation apparatus free of thermo-forces in accordance with DIESELHORST and provided by O. WOLFF. Enclosing the wires

TABLE I.

| Datum. | Tl—VIII—1916. | Tl.—IX—1916. |
|-------------------|---|----------------------|
| 5 January 1917. | | 1.149 ₀ Ω |
| 6 January 1917. | 4.439 Ω | |
| | Immersed in liquid air. | |
| 8 January 1917. | 4.441 ₅ Ω | |
| | Immersed in O ₂ liq. and H ₂ liq. | |
| 30 January 1917. | | 1.150 ₇ Ω |
| 2 February 1917. | 4.447 ₅ Ω | . |
| 6 February 1917. | 4.448 Ω | 1.150 ₅ Ω |
| 13 February 1919. | 4.446 Ω | |
| 19 February 1919. | 4.446 Ω | |
| 20 February 1919. | . | 1.150 ₂ Ω |

in an atmosphere of helium proved to be completely sufficient; the results of the zero point determinations are found in Table I (see p. 444). The zero point measurements are partly due to Dr. J. M. BURGERS, now Professor at Delft.

§ 3. *Measurements in liquid helium; determination of the vanishing point temperature.* The resistances were placed in the cryostat provided with a stirring apparatus shown in Comm. N°. 124c, fig. 4. For determining the amount of their resistance the second method mentioned in § 2 was used. The measurements were always made with both directions of current in the circuit of the resistances, care being taken that to each of them the direction of the current in the compensation apparatus corresponded. Moreover, in measurements below the vanishing point temperature the galvanometer was observed when the current was reversed in the circuit of the resistances only (this betrays super-conductivity more quickly): in the case of super-conductivity there must be no change of position observable.

The temperatures are determined by the measurements of the vapour pressure of the helium bath, the connection between pressure and temperature having been derived graphically from the results in Comms. N°. 119 and N°. 147b. Close to the vanishing point temperature the pressure of the bath was followed with the kathetometer (June 5th 1919); we give below the diagram of a series of observations (in this field of temperature 1 m.m. pressure = about 0.01 of a degree).

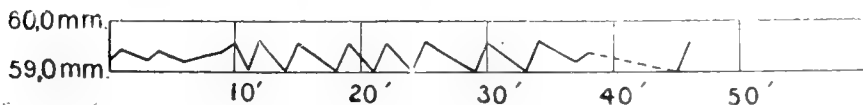


Fig. 1.

In spite of the fact that the wires were not in contact with the liquid helium, in the measurement of their resistances the galvanometer reacted with surprising rapidity to the changes of temperature of the bath. The results are given in Table II.

From Table II it appears that a constant difference Δw exists for all temperatures; in spite of this additive resistance¹⁾ of *T'-VIII-1916* with regard to *T'-IX-1916* both become super-conducting at the same

¹⁾ If this additive resistance is taken constant, it becomes $0,00083 W_0 = 0,0037 \Omega$; we must assume in the meantime that it is largely due to the joint.

temperature. The behaviour of *Tl*-VIII confirms the experience gained with *Pb*-wires (Comm. N°. 133*d* § 15), that joints in a wire do not affect its becoming super-conducting. The unsteadiness of the resistance at 2°.33 K. is caused by the pressure variations of the bath over a range of 0.6 m.m. Hg, corresponding to 0.006 of a degree;

TABLE II.

| P_{Helium} in local m.m. Hg. | T . | $W_{\text{Tl-VIII-1916}}$ | $W_{\text{Tl-IX-1916}}$ | $w_{\text{Tl-VIII}} = \left(\frac{W}{W_0}\right)_{\text{Tl-VIII}}$ | $w_{\text{Tl-IX}} = \left(\frac{W}{W_0}\right)_{\text{Tl-IX}}$ | $\Delta w = W_{\text{Tl-VIII}} - W_{\text{Tl-IX}}$ |
|---|------------|---|---------------------------------------|--|--|--|
| | 273°.09 K. | 4.446 Ω | 1.150 ₂ Ω | 1.00000 | 1.00000 | |
| | 4.24 | 0.0075 | 0.0009 ₆ | 0.0016 ₈ | 0.0008 ₄ | 0.0008 ₄ |
| | 3.33 | 0.0069 | 0.0008 ₃ | 0.0015 ₅ | 0.0007 ₂ | 8 ₃ |
| 80.— | 2.49 | 0.0067 | 0.0007 ₉ | 0.0015 ₁ | 0.0006 ₉ | 8 ₂ |
| 70.— | 2.42 | 0.0067 | | 0.0015 ₁ | | |
| 65.— | 2.38 | 0.0066 ₅ | 0.0007 ₈ | 0.0015 ₀ | 0.0006 ₈ | 8 ₂ |
| 60.— | 2.34 | 0.0066 | 0.0007 ₆ | 0.0014 ₉ | 0.0006 ₆ | 8 ₃ |
| 59.3 | 2.33 | swings from 0.006 ₆ to 0.002 | swings from 0.0007 about 0.0007 | swings from 0.0014 ₉ to 0.0004 ₅ | swings about 0.0006 | |
| 58.6 | 2.33 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | |

in this field of temperature thallium is in the same condition as is shown for mercury in Comm. N°. 133a p. 24, fig. 6. At a current

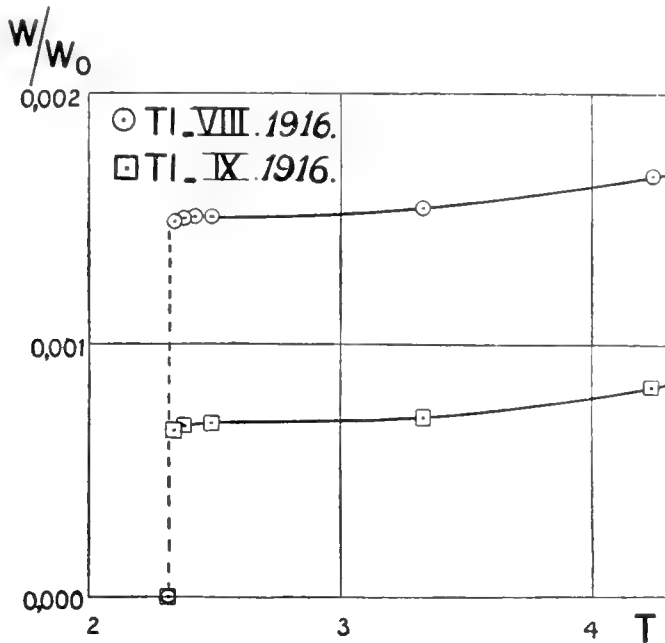


Fig. 2.

strength of 3,1 m.A. through the resistances the resistance falls, thus, within a smaller temperature range than in mercury; a similar difference had been found earlier between mercury and tin.¹⁾ At $T = 2^{\circ}.32$ K. all measurable resistance has disappeared.

§ 4. *Highest limit of a microresidual resistance.* This limit is found from the quotient of the smallest observable potential difference and the threshold value of the current, it being assumed that OHM's law still holds. We found:

15 April 1919, for *Tl-VIII* $\frac{W}{W_{273^{\circ}.K.}} < 14 \cdot 10^{-10}$ at $p = 2.3$ m.m. Hg and

27 May 1919, for *Tl-IX* $\frac{W}{W_{273^{\circ}.K.}} < 24 \cdot 10^{-10}$ at $p = 2.6$ m.m. Hg.

The difference in the results may be due to the inequality of temperature, but more to the difference of current threshold value of the two wires (see further § 5). If the value $\frac{W}{W_{273^{\circ}.K.}}$ for thallium

¹⁾ This comparison is defective, for as yet the fall of resistance in mercury, tin and thallium not has observed on wires of the *same* diameter by using the *same* strength of measuring current. [Note added in the translation.]

is compared with that for other super-conductors (Comm. N^o. 133d, p. 67) the retrogression of the limit caused by a greater decrease of temperature below the vanishing point temperature would seem to be recognisable in the measurements of wires of different metals, as has been ascertained already by measurements of one wire of one metal. But we must point out that this general conclusion cannot be drawn before the value of the threshold current as a function of $T_{\text{vanishing point}} - T$ and of the dimensions of the wire is known and after it has been ascertained whether a returning resistance is due to a single "bad place", or whether it is distributed over the whole length of the wire.

§ 5. *Threshold value.* At some temperatures we tried to determine the threshold value of the current, that is the strength of the current sent through the wire, which again generates a measurable potential difference. The results are given in Table III.

The two first observations in Table III show that for wires of different diameter at the same temperature the quantity $\frac{i}{r}$ seems to be much more a constant than the current density. The latter quantity occurs in the expression for the magnetic field at the surface of the wire through which a current passes.

F. B. SILSBEE¹⁾ drew special attention to the influence of this field. The determination of the threshold value of the magnetic field for thallium by means of external fields, and the comparison of it with H , derived from the two first observations in Table III by means of $H = \frac{2i}{r}$, (the wires *Tl-VIII* and *Tl-IX* therefore being regarded as straight), must prove whether these two strengths of field are equal, and that therefore the magnetic field is the primary factor in the disturbance of super-conductivity. Then the "bad places" referred to more than once, are the places with the smallest diameter; the returning of the resistance caused by the current, occurs first in these places only. The above mentioned experiment with thallium is prepared and also a similar one on a more extensive scale with the more easily manipulated tin; it must not be forgotten, that at the return of the resistance at great strengths of current such a development of heat soon takes place, that first the wire and if this melts the galvanometer is in danger; this makes the determination of large current threshold values rather risky.

¹⁾ F. B. SILSBEE, *Scient. Pap. Bur. of Stand. No. 307* (1917).

TABLE III. 2)

| Date. | Resistance. | Diameter in m.m. | Section in m.m. ² | p_{He} in m.m. local Hg. | Tempera- ture 1) | Threshold value in amp. | Current density in Amp. per m.m. ² | i in Amp. r in m.m. |
|---------------|--------------|---------------------|---------------------------------|--------------------------------------|---------------------|-------------------------------|--|----------------------------|
| 25 April 1919 | Tl-VIII-1916 | 0.2 | 0.031 | 2.3 | 1.3 ₆ K. | 1.5 ₇ | 50.0 | 15.7 |
| 27 May 1919 | Tl-IX-1916 | 0.5 | 0.196 | 2.6 | 1.3 ₈ | 3.6 ₀ | 18.4 | 14.4 |
| » | » | » | » | 55 à 56 | 2.29 | 0.25 ₂ | 1.3 | 1.0 |
| 5 June 1919 | » | » | » | 54 | 2.28 | 0.62 ₅ | 3.2 | 2.5 |
| » | » | » | » | 58 | 2.31 | 0.12 ₆ | 0.6 | 0.5 |

1) The two first temperatures in this table are derived graphically by means of a formula slightly differing from that given in Comm. No. 159 in the „Discussion”.

2) Referring to § 3 concerning the heat conductivity of helium vapour, yet the threshold values might have been found greater, when the resistances would have been surrounded *directly* by liquid helium. [Note added in the translation].

If we assume, that in super-conductivity the current runs only in an extremely thin layer at or along the surface of the wire and that each element of a section of this layer ceases to be super-conducting at a certain current saturation dependent upon the temperature, integration over the whole layer yields the threshold current and for wires of different diameter we get the constancy of $\frac{1}{r}$. The assumption of current saturation along the surface does not, however, explain the connection, suggested by SHLSBEE, between the threshold values of the current and the magnetic field.

Physics. — “*Further experiments with liquid helium. R. On the electric resistance of pure metals etc. XI. Measurements concerning the electric resistance of ordinary lead and of uranium lead below 14° K.*” (Comm. N°. 160*b* from the Physical Laboratory at Leiden). By Prof. H. KAMERLINGH ONNES and W. TUYN.

(Communicated at the meeting of October 28, 1922.)

§ 1. *Object of the research. Method of preparing the resistances.*

In Comm. N°. 133*d* § 13*β* we reported that “Kahlbaum” lead became superconducting at the boiling point of liquid helium, and remained so at 4,°3 K., the highest temperature attainable with the usual cryostat for liquid helium; in § 15 of the same Comm. from the threshold value of the current at 4,°25 K. the vanishing point temperature was estimated at about 6° K. The object of the investigation described below was to establish the vanishing point temperature of lead more accurately, as well as to trace the difference in the vanishing point temperature of lead and uranium lead (*Ra G*) and to follow the course of the change in the resistance of lead with the temperature above the vanishing point, if possible up to 14°,0 K, the lowest liquid hydrogen temperature. Regarding a possible difference of vanishing point temperature for isotopes it seemed not impossible that the occurrence of the superconductivity might be influenced by the mass of the nucleus.¹⁾

For the preparation of the resistances we used “Kahlbaum” lead and uranium lead (*Ra G*), of which Prof. HÖNIGSCHMID of Vienna very kindly put 16,5 gr. at our disposal; the atomic weight of ordinary lead from non-radio-active sources is 207,20, that of *Ra G* from BRÖGGERIT used is 206,06²⁾. Wires were drawn from both kinds of lead and resistances prepared from them in the manner described in § 1 of Comm. N°. 160*a*; the chemical properties of the metal

¹⁾ Concerning the properties of isotopes see the article by K. FAJANS in the *Elster-Geitel-Festschrift* (Vieweg) and the Presidential Address to the American Association at Baltimore, Dec. 1918 by T. W. RICHARDS.

²⁾ According to a letter from the firm of May 17th, 1916, “Kahlbaum” lead contains a trace of Cu and Fe, the total impurity is less than 0,01%; in a letter of Dec. 8th, 1916 they give a more precise calculation of impurity: 0,002% Cu and Fe. For an account of the atomic weight of lead isotopes cf. F. W. ASTON “*Isotopes*”, London 1922.

made it possible to extend less care on them than on the preparation of the T^l -resistances, so that it is not necessary that the resistances should be shut off from the air in a glass tube with helium gas. We used the resistances *Pb-1919-B*, diameter 0,5 m.m. not enclosed in a helium atmosphere, *Pb-1919-I*, diameter 0,12 m.m. enclosed in a helium atmosphere and *Isotope Pb-1919-I*, in dimensions as much as possible the same as *Pb-1919-I* and treated in the same way.

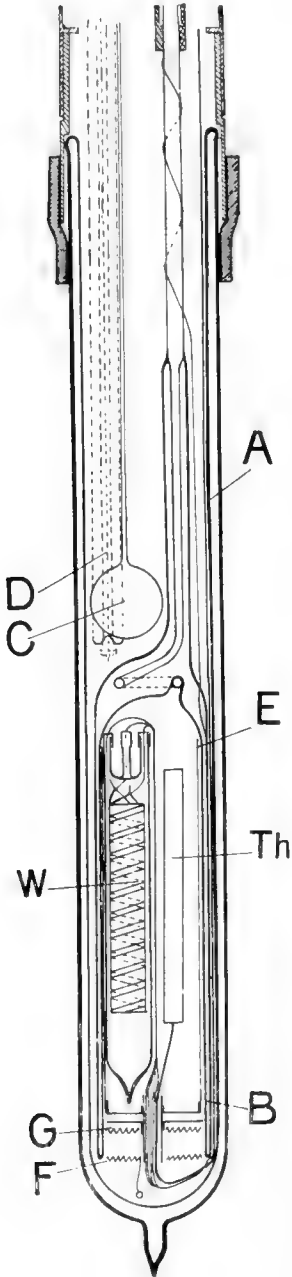


Fig. 1.

§ 2. *Arrangement of the cryostat.* The cryostat with which the experiments were made, is executed by and under the supervision of the chief of the Techn. Dep. of the Cryog. Lab., Mr. G. J. FLIM. Roughly speaking, it is the same as that described in Comm. N^o. 1246. A characteristic of the present cryostat is that objects to be measured are surrounded by helium vapour or gas (the latter at very low temperature); by using it, the temperature field between the boiling point of helium ($4^{\circ},2$ K.) and the lowest temp. obtainable with liquid hydrogen ($14^{\circ},0$ K.) is bridged over for the first time. For the arrangement see fig. 1. In the entirely silvered vacuum glass *A*, an also entirely silvered vacuum glass *B* hangs in an inverted position, ending in a single silvered glass tube; the bell-shaped space inside this glass is the experimental chamber. In this space are found the resistances (in fig. 1 there is only one, marked *W*) and the helium-gas-thermometer *Th*. The upper end of *B* opens out outside the cryostat and is connected with the gasholder; *B* is there provided with a regulating tap *K* for blowing off (not visible in the drawing). The liquid helium comes in through the entrance *D*; the floater *C* shows the height of the helium level. If the tap *K*, leading to the gasholder, stands open, the helium will fill both *A* and *B*; at the beginning of the experiment measurements can thus be made at the boiling point of liquid helium. If the

tap *K* is closed, the helium vapour formed will quickly drive the liquid helium out of the bell-shaped cryostat space; by opening the tap *K* and putting on the electric heating in the spiral *F*, a constant vapour stream may be sent through the cryostat; the stream may be brought to the temperature desired by electric heating of the spiral *G*; thus the liquid level of the evaporating helium remains between *F* and *G*. The copper mantle *E* inside the bell contributes to the acquiring of an even temperature over the whole space; further experiments must show in how far uniformity of temperature has been achieved with the arrangement as described. The first cooling uses a great deal of liquid helium.

§ 3. *Resistance and temperature determinations.*

The resistances are measured by comparison of the deflections of the galvanometer, when connected with the extremities of an unknown and a known resistance (0,001 or 0,01 Ω O. WOLFF); the resistances are proportional to the means of the deflections for both directions of the current, as follows from the comparison of the deflections for 0,001 and 0,01 Ω .

The temperatures are determined with a heliumgasthermometer of constant volume and with open manometer, the height of the barometer is read from an aneroid. In the measurements of May 18th 1920 the zero pressure of the thermometer was calculated to be about 1140 c.m.; as it was not easy to determine this pressure accurately, the pressure at the temperature of liquid helium was taken as calibration point (this temperature followed from the vapour pressure of the bath).

For the measurements of May 28th 1920 the zero-pressure of the thermometer was decreased to 290 cm., in order to have less difficulty with the corrections on the provisional international Kelvin scale, these corrections in and below the field of liquid hydrogen being insufficiently known. As two calibration points the tensions of the thermometer served, placed in liquid helium (May 28th 1920) and in liquid hydrogen (May 29th 1920); the temperatures of these points again follow from the vapour pressure of the bath, using the data from Comm. N°. 147*b* and N°. 156*b*.

For the correction of the indications of the thermometer on the provisional international Kelvin scale, we had at our disposal the data of Comm. Suppl. N°. 34*a*, p. 17, note 4 (obtained from the data of Comm. N°. 102*c*), in which $B_{-254^{\circ}\text{C}}$ has been taken zero,

TABLE I.

| Temp. | B. | | $\Delta t^1)$ (Pressure heliumthermometer at 0° C. = 1000 m.m.) | |
|----------|-------------------|------------------|--|---------------------|
| | Old observations. | New observations | Old observations. | New observations. |
| 20°.5 K. | | - 0.00010 | | + 0.04 ₅ |
| 19.1 | 0.00000 | | + 0.03 ₉ | |
| 4.29 | - 0.00305 | | + 0.05 ₁ | |
| 4.22 | | - 0.00347 | | + 0.05 ₂ |
| 3.71 | | - 0.00420 | | + 0.05 ₃ |
| 3.44 | | - 0.00538 | | + 0.05 ₇ |

Further we have made use of the newly calculated Δt 's, and from this we deduce table II.

TABLE II.

| Filling I. $p_0^{\circ}C = 1140$ c.m. May 18, 1920. | | Filling II. $p_0^{\circ}C = 290$ c.m. May 28 and 29, 1920. | | | |
|---|------------|--|---------------------------|-----------------------|---------------------------|
| $T_{\text{vapour tension}}$ | Δt | $T_{\text{He, uncorrected}}$ | $\frac{p}{T_{\text{He}}}$ | p in local m.m. Hg. | $\frac{p}{T_{\text{He}}}$ |
| 4.20 K. | 0.60 | 3.60 | 42.1 ₆ | 209.7 | 10.3 ₆ |
| | | | | 42.7 | 10.4 ₈ |

¹⁾ $\Delta t = (T - T_0) \left(\frac{T_{100} B_{100} - T_0 B_0}{100 v} \right) - \left(\frac{T B T - T_0 B_0}{v} \right)$, in which v is the volume of gas in the thermometer, expressed in the theoretic normal volume; the C 's may, according to calculation, be neglected even with a large density.

and also from Comm. N°. 119 § 5b $B_{4^{\circ}, 2^{\circ}\text{K.}} = -0,000047^1$); Table V of Comm. N°. 156a gives a resumé of the corrections, calculated with the above data. In accordance with note 1 and 3, p. 27, Comm. N°. 156a here $B_0 = 0,000499$, $B_{100} = 0,000476$, $\alpha_{\text{He}} = 0,0036614$ are taken, and the influence of the C 's is neglected²⁾.

New determinations, to be published shortly, of helium isotherms at $T = 2^{\circ}, 5$, $4^{\circ}, 2$, $3^{\circ}, 7$ and $3^{\circ}, 4$ K. gave provisional new values for B , which therefore infer the introduction of different corrections in the provisional intern. Kelvin-scale; they are larger than those in Table V, Comm. N°. 156a and they do not come into line so well with those for higher temperatures. For the sake of completeness we give a comparison of these in Table I. (cf. p. 387).

§ 4. *Temperature of the vanishing point.* On May 18th and 28th 1920 all three resistances proved superconducting in liquid helium and behaved, therefore, in the usual way. After this the cryostat was gradually brought to a higher temperature by electric heating of the vaporised helium. At a certain moment the galvanometer moved quickly over 35 c.m. on the scale and the vanishing point was apparently reached; the suddenness of the deflection speaks well for the usefulness of the cryostat if not too high demands are put upon it. A repetition of the heating (very gradually) confirmed the first result. While the temperature was kept constant the thermometer was read at the vanishing point. The results are given in Table III.

TABLE III.

| Data. | Filling. | p_{gas} thermom. in local m.m. Hg. | T_{He} , uncorrected | $\angle t.$ | $T.$ |
|---------------|----------|---|-------------------------------|-------------|---------------------|
| May 18, 1920. | I | 263.6 | 6.2 ₅ | 0.58 | 6.8 K. |
| May 28, 1920. | II | 73.9 | a. 7.0 ₈ | 0.15 | a. 7.2 ₃ |
| | | | b. 7.1 ₃ | 0.15 | b. 7.2 ₈ |

¹⁾ The $B = -0,000047$ is that derived according to $pv = RT + \frac{B}{v}$; the B 's further mentioned in this number are those according to $pv = RT \left(1 + \frac{B}{r}\right)$, in agreement with the change of notation mentioned in note 360 of Comm. Suppl. N°. 23.

²⁾ These values for B_0 , B_{100} and α_{He} must be retained to get the corrections on the provisional internat. Kelvin-scale. Measurements have shown that it would have been more correct to use $B_0 = 0,000513$, $B_{100} = 0,000492$ and $\alpha_{\text{He}} = 0,0036613$ (Comm. N°. 102b, Table I and Com. N°. 156a, p. 22, note 1); this would lead to a *second* provisional intern. Kelvin-scale (helium-Avogadro-scale) for which reason we retain the first B 's.

In filling II a is calculated by interpolation between calibration points $20^{\circ},24$ and $4^{\circ},07$ K., b by using only the calibration point $20^{\circ},24$ K. in the same way as in filling I only calibration point $3^{\circ},60$ K. needed to be used.

The agreement between the measurements with filling I and II is bad. If in filling II we calculate, with the pressure increase of $10,3^{\circ}$ mm. per degree, the temperature of the helium on May 28th, 1920, the calculation yields $4^{\circ},27$ K, while the vapour pressure gave $4^{\circ},22$ K (table II); this is in favour of the measurements on May 28th. If we further take the large Δl 's in filling I into consideration, a determination with filling I deserves less confidence than one with filling II. We take T vanishing point lead = $7^{\circ},2$ K, although it is still desirable to make a more accurate determination.

§ 5. *Comparison of the vanishing point temperatures of lead and uranium lead (Ra G).*

On May 18th, 1920 the cross-thread of the kathetometer was adjusted to the mercury meniscus in the open tube of the thermometer at the pressure belonging to the vanishing point temperature of *Pb-1919-I* (the meniscus in the closed tube must of course always be kept on the same mark).

After a decrease of temperature *Isotope Pb-1919-I* was inserted in the resistance circuit and the temperature again raised. If the galvanometer moved, because the resistance passed through the vanishing point, the meniscus in the tube of the thermometer passed the cross thread; this phenomenon was certain up to 1 mm. Hg: "*Kahlbaum*" lead, atomic weight 207,20 and uranium lead (*Ra G*), atomic weight 206,06 have the same vanishing point temperature within the accuracy of $\frac{1}{100}$ degree. The same result was yielded by *Pb-1919-B*; an influence of the smaller current density in consequence of the larger diameter could not be detected (the strength of the measuring current was always 7,8 m.A.).

§ 6. *Resistances above the temperature of the vanishing point.*

The results of these measurements are given in fig. 2; the point most to the right, placed within a square, is the result of a measurement in liquid hydrogen. As vanishing point $7^{\circ},2$ K was taken. To make the curve join on properly to the one in the field of liquid hydrogen it must be traced as in the diagram; that is why correspondence with the points marked is defective. The broken crosses have the following meaning: if the difference between the vanishing

point temperatures found on May 18th and May 28th may be attributed entirely to Δt having been taken too large on May 18th, all the other temperatures must be recalculated, this recalculation yields the crosses. Although this approximation is theoretically not quite correct, as $T - \Delta t$ and not T ought to rise at every temperature in the same ratio, yet the results are in favour of the suggested assumption.

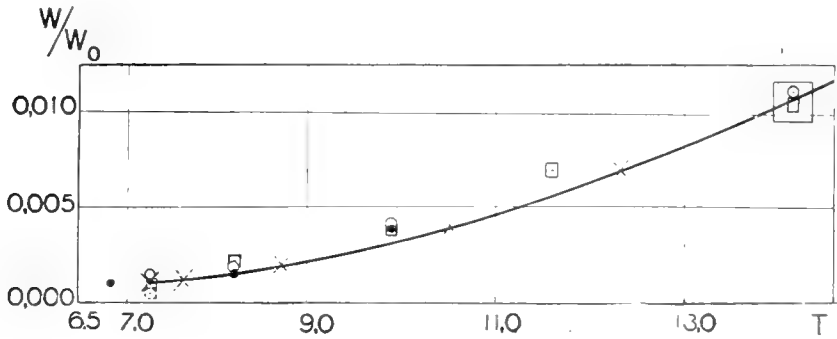


Fig. 2.

- *Pb*-1919-*I*,
 - ⊙ *Isotope Pb*-1919-*I*,
 - ⊕ *Pb*-1919-*B*,
 - *Pb*-1919-*B*,
 - ×
- } 18 May 1920.
- } 28 May 1920.
- × Reduced observations : § 6.

Chemistry. — “*The Action of Sodiumamide on Pyridine, and some Properties of α -aminopyridine*”. By J. P. WIBAUT and ELISABETH DINGEMANSE. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of December 30, 1922).

Through TSCHITSCHIBABIN's¹⁾ beautiful researches α -aminopyridine has become easily accessible. This investigator found that sodium amide acts on pyridine as follows:



On decomposition of the reaction product with water, aminopyridine and sodium hydroxide is formed.

As we required this substance as starting material for synthetic investigations, we have applied the method of preparation found by TSCHITSCHIBABIN. Though also in our experiments α -aminopyridine was formed as chief product, we found other substances than the Russian investigator among the by-products.

We experienced that the action of sodium amide on pyridine can take place in different ways, dependent on the nature of the sodium amide preparation used. We have prepared sodium amide according to TITHERLEY'S indication by the action of carefully dried ammonia on melted sodium at 350—400° C. The preparation obtained was a pure white, showed a crystalline fracture, and contained no free sodium. This preparation did not react with pyridine. A preparation prepared at 300°, reacted very slowly with pyridine. In this experiment very little α -amino pyridine was however, formed; further a little γ - γ -dipyridyl, and some other products, which we did not examine.

A sodium amide preparation of KAHLBAUM, which was pretty impure, as it contained free sodium and also sodium hydroxide, acted vigorously on pyridine, as TSCHITSCHIBABIN states. Another preparation of KAHLBAUM, which was apparently much purer, acted in exactly the same way. A mol. of pyridine is diluted with toluene, and this mixture is heated with a mol. of finely powdered sodium amide at 120—125° for seven hours.

¹⁾ Journal de la Société Physico-Chimique Russe, **46**, 1216 (1914).

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We have decomposed the reaction product with water according to TSCHITSCHIBABIN's direction, dissolved it in ether, and distilled it at a pressure of 15 m.m. The bulk went over at 104—125°, and was almost pure aminopyridine in agreement with the records of the investigator mentioned. At 130—180° and 15 m.m. an oil distilled, which soon gets a dark colour when exposed to the air. After some time white crystals separated out of this oil. Recrystallized out of water these crystals became colourless, long needles melting at 73°. This substance is the hydrate of γ - γ -dipyridyl, which has already been described by ANDERSON. After drying in a vacuum exsiccator we obtained the γ - γ -pyridyl itself, which melts at 112°. We identified this substance by analysis and by oxidation with potassium permanganate. We obtained white crystals melting at 307°, which agrees with the melting-point of iso-nicotinic acid. On action of picric acid on γ - γ -dipyridyl, both dissolved in alcohol, we obtained a picrate crystallizing in fine yellow needles, and melting at 252°. As appears from analysis this picrate contains 1 mol. of picric acid to 1 mol. of γ - γ -dipyridyl. With anhydrous acetic acid and zinc dust the γ - γ -dipyridyl gave the intensive violet colour reaction, which was lately described by DIMROTH and HEENE.

There are still some more substances to be found in the oil that distilling at 130—180° and 15 m.m. pressure. After the bulk of the γ - γ -dipyridyl had been removed from this oil, we treated the liquid with hydrochloric acid. Two chlorides were then obtained, which both crystallized in white needles. After recrystallisation from diluted hydrochloric acid one melted at 115—116°; the second melted above 280°. The latter substance appeared to be the salt of γ - γ -dipyridyl.

We have liberated the base from the chloride of 115—116°, and obtained white crystals melting at 94—95°. This melting-point agrees with the α - α -dipyridyl-amine ($C_8H_8N_2$),NH, which was obtained by STEINHÄUSER and DIEPOLDER¹⁾ from α -chloro pyridine and α -amino pyridine by heating with barium oxide.

The nitrogen percentage of our crystals, which melt at 94—95°, agrees with the value calculated for dipyridyl amine.

TSCHITSCHIBABIN says that this dipyridyl amine is formed through the action of two molecules of pyridine on 1 mol. of sodium amide, but does not yet describe the experiments from which this appears. When speaking of the action of 1 mol. of pyridine on 1 mol of sodium amide (the same way as we performed the reaction TSCHIT-

¹⁾ Journ. f. prakt. Chem. 93, 393 (1916).

SCHIBABIN does not mention the dipyridyl amine. He prepared the dipyridylamine from α -chloropyridine and α -aminopyridine by heating with zinc chloride, and gives as meltingpoint 86—87°.

We have prepared a picrate from the dipyridylamine, which melts at 227°.

Our observations on the melting-points of dipyridylamine itself, on the salt with hydrochloric acid, and on the picrate of this base are in perfect harmony with STEINHÄUSER and DIEPOLDER's records, so that we have no reason to doubt the identity of our preparation.

The investigation of the components of the oil that goes over at 130—180° and 15 m.m. pressure, was not yet completed then, for a large part of this oil remained liquid after treatment with hydrochloric acid. We removed the hydrochloric acid from this liquid part, and then distilled the oil at ordinary pressure. We collected three fractions, viz. of 293—295°, of 295—300° and above 300°. The first two fractions had a nitrogen percentage of 13.9%; the fraction above 300° had 16.4% of nitrogen. From this last fraction a little dipyridylamine was still deposited. The first two fractions were joined; this liquid appeared to be strongly unsaturated: it immediately decolours a solution of permanganate and soda at ordinary temperature. We have subjected part of this liquid to the oxidation with sodium permanganate in sulphuric acid solution. A white substance, which crystallized in white leaves and melted at 74°, could be isolated. The nitrogen percentage of it was 8.0%. This shows that it cannot be a dipyridylamine or a dipyridyl.

Besides these crystals, a viscid liquid was obtained from the oxidation product. The investigation of these substances is being continued.

It appears from all this that on action of sodium amide on pyridine there are formed, besides aminopyridine, several other pyridine derivatives, among which the γ - γ -dipyridyl seems to preponderate quantitatively. TSCHITSCHIBABIN likewise observed by-products in the reactionproduct which arises from sodium amide and pyridine. After the α -aminopyridine had been distilled off, he states that an oil went over which distilled at 120—180° and at 15—20 m.m., and besides a fraction that went over at 180—250° and 15—20 m.m.

From the fraction of 120—180° crystals are deposited which, after recrystallisation from benzene, melted at 158°. TSCHITSCHIBABIN supposed these crystals to be γ -aminopyridine, but he could not identify the substance for want of material. From the oil distilled at 180—250° this investigator isolated the α - α' diaminopyridine; there were also other substances present, which he did not identify.

In many experiments we prepared some hundreds of grammes of amino pyridine; the reaction always proceeded as we described above. We never observed a substance with a melting-point of 158° ; nor did we ever observe a diamino pyridine.

Accordingly the action of sodium amide on pyridine can evidently give rise to the formation of different substances. We have not been able to find out why with some sodium amide preparations amino pyridine was not formed. Addition of small quantities of water or free sodium had no influence on this. We also caused sodium to act on a mixture of pyridine and toluene, both at the ordinary temperature and at the temperature of boiling. In this case there was formed a tough amorphous mass, insoluble in water and in organic solvents, soluble in acids. By extraction with ether we could isolate only a small quantity of $\gamma\text{-}\gamma$ -dipyridyl. This result is in accordance with the early experiments of ANDERSON.

The formation of the important quantities of $\gamma\text{-}\gamma$ -dipyridyl in our amidisation seems, therefore, not to be in connection with a possible percentage of sodium in the sodium amide preparation used.

As amino pyridine seems comparable with aniline, we examined the action of oxidizers on this pyridine base. For so far as we know, nothing is known about this.

Bichromate and diluted sulphuric acid change a diluted solution of amino pyridine only slowly at ordinary temperature. When the mixture is left standing for some days, the liquid gets dark. From this solution an amorphous green substance is isolated, insoluble in water, alcohol, and ether, soluble with emerald green colour in diluted hydrochloric acid. On evaporation of the hydrochloric acid an amorphous blue substance was left behind. At 90° the action of sulphuric acid and bichromate on amino pyridine takes place more violently; and amorphous products are also formed. In these experiments part of the amino pyridine however remained unchanged.

The action of potassium bichromate in acid solution on this base takes place much less rapidly than in case of aniline.

The action of potassium permanganate proceeds in an entirely different way. Amino pyridine is rapidly changed by permanganate in acid solution; after a few minutes all the permanganate has disappeared. When a diluted solution of amino pyridine is added to a diluted permanganate solution containing soda, a slow action takes place. When, however, first a neutral permanganate solution is added to a diluted solution of amino pyridine, and then a few drops of 10% sodium hydroxide, a change of colour is immediately seen. When we start from a 0.1% solution of amino pyridine, the

liquid first becomes dark violet, then pure blue, after a few minutes the colour has become emerald green. This green colour does not change again, when there is no excess of permanganate present. If the solution of the amino pyridine is somewhat more concentrated, the green colour at once sets in after a transient dark colouring.

This reaction is characteristic of amino pyridine and very sensitive. In acetyl amino pyridine this colour reaction does not set in at the ordinary temperature until after some hours, soon however on boiling.

Whether the acetyl rest is split off primarily here, has not yet been examined.

A more detailed account of the observations discussed briefly here will be published in the *Recueil des Travaux chimiques*.

Physics. — “*On Centres of Luminescence and Variations of the Gas Pressure in Spectrum Tubes at Electrical Discharges*” II. ¹⁾
By Dr. L. HAMBURGER. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of October 28, 1922).

§ 1. *Introduction.*

Experiments made by the author in 1916 showed that continuous current-discharges when passing through not too rarefied gases, gave rise to differences of pressure, the value of which, with sufficient current density can amount to thirty per cent of the total pressure. A first communication on this subject appeared in the author's thesis for the doctorate in the beginning of July 1917 ²⁾. In these investigations such variations of pressure were observed in numbers of gases of very different natures, as argon, neon, helium, nitrogen, hydrogen; it was found that the effects observed are very great in argon, hardly perceptible in hydrogen, and it was seen that the pressure effect must increase with the intensity of the current (loc. cit. p. 94), and with the root of the molecular weight (loc. cit. p. 107).

Four months after the publication of this Thesis for the Doctorate F. SKAUPY ³⁾ published a short paper, in which he mentioned differences of pressure in continuous current discharges observed by him (only) in the case of noble gases; these differences of pressure were small compared with the effect found by us owing to the small current density applied by him.

In April 1920 the author of this communication ¹⁾ published some further theoretical views and quantitative calculations about the effects found, F. SKAUPY confining himself in the course of the same year to some qualitative remarks ⁴⁾, which indeed referred more to the phenomenon of electro-striction, which in our opinion can only play a subordinate part.

Finally in the middle of 1922 there appeared a publication by A. RÜTTENAUER ⁵⁾ on an important experimental investigation, in

¹⁾ Cf. for I: L. HAMBURGER, These Proc. Vol. XXIII N^o. 2 and 3, p. 379.

²⁾ L. HAMBURGER, Thesis for the doctorate, Delft 1917. Cf. These Proc. 20, 1043 (1917). Zeitschr. f. Wissensch. Phot., 18, 1 ('19).

³⁾ F. SKAUPY, Verh. d. Deutsch. Phys. Ges. 19, 264-'67. Nov. Heft, '17.

⁴⁾ F. SKAUPY, Zeitschr. f. Physik 2, 215. Aug. Heft, '20.

⁵⁾ A. RÜTTENAUER, Zeitschr. f. Physik 10, 269-274 ('22).

which the variations of pressure of noble gases were subjected to a closer examination and the dependence of the effects found on different variables was given in an approximative "empirical" formula.

§ 2. *Purpose.*

After having thus established our priority, we set ourselves the task:

1st. to show that the experimental results obtained by A. RÜTTENAUER in his extension of the investigations on the pressure effect correspond to the theoretical formulae developed by us in I, in which also the practical part of RÜTTENAUER's empirical formula is included;

2nd. to prove that serious objections may be raised against SKAUPY's theoretical view of the pressure effect;

3rd. to draw further conclusions from RÜTTENAUER's important determinations, also in connection with our earlier data on this subject, and our objective, quantitative determinations on light emission in continuous current discharges in spectrum tubes likewise published in our Thesis.

§ 3. *Formula for the calculation of the pressure-effect.*

RÜTTENAUER gives the empirical formula:

$$\Delta p = f \frac{Ag \sqrt{M}}{p} \cdot \frac{l}{Q}$$

in which Δp represents the difference of pressure found, f a constant, A the current density, g the gradient of tension, M the molecular weight, p the total gas pressure, l the length of the pos. pile, Q its cross section.

It is seen from this that RÜTTENAUER finds experimentally that the pressure effect would be in inverse ratio to the total gas pressure¹⁾, whereas the author of this paper found — also experimentally — that with not too great variations of p , Δp varied little, if at all, with p .²⁾

How is this difference in result to be accounted for?

¹⁾ Which was, indeed, also mentioned by F. SKAUPY in his first publication (1917).

²⁾ RÜTTENAUER is erroneously of opinion that it would have been found both by me and by SKAUPY that in argon the pressure effect is in inverse ratio to the gas pressure. It was on the contrary observed by us that within certain limits the pressure effect showed a very slight variability with regard to the gas pressure.

On comparison of RÜTTENAUER'S researches with ours it appears that we made use of comparatively narrow capillary tubes as circuit of the current, the German investigator on the other hand of comparatively wide tubes. We derived, however, already before, that two different formulæ must be valid for these cases, and this as a consequence of the fact that in the case of wide tubes the laws of POISEUILLE should be applied when taking the diffusion phenomena into account, for narrow tubes those of KNUDSEN-LANGMUIR. For in the first case the electric mass-transportation $c_1 \frac{A Q^{1/2}}{a p}$ may be put equal to:

$$c_1 \frac{D^2}{l} (p_2 - p_1) \sqrt{\frac{T^2}{M} *)}$$

in the second case to:

$$c_2 \frac{D^3 p_2 - p_1}{l p} \sqrt{\frac{T^2}{M} *)}$$

In the first case the theoretical formula for the pressure effect — taking into account that $Q = \frac{\pi D^3}{4}$ for tubes with round cross-section — is equal to:

$$p_2 - p_1 = \Delta p = f_1 \frac{A Q}{a p} \frac{l}{D^2} \sqrt{M} = f_1 \frac{A}{a p} \cdot \frac{l}{Q} \sqrt{M} . . . (I)$$

in the second case to:

$$\Delta p = f_2 \frac{A Q}{a} \cdot \frac{l}{D^3} \sqrt{M} = f_2 \frac{A}{a''} \cdot \frac{l}{D} \sqrt{M} . . . (II)$$

in which

$$f_1 = \frac{c_1}{c_2 \sqrt{T}} , f_2 = \frac{c_1}{c_1 \sqrt{T}} , a' = a \cdot \left(\frac{4}{\pi}\right)^2 \text{ and } a'' = a \frac{4}{\pi}$$

When on grounds to be given later, the gradient g is taken inversely proportional to a , we may write equations I and II as follows:

$$\Delta p = f \frac{A g}{p} \cdot \frac{l}{Q} \sqrt{M} (III)$$

resp.

¹⁾ In which c_1 is a constant. Compare further Equation 9, p. 390, These Proc. XXIII, No. 2 and 3. The factor Q has been introduced, because A now denotes current density, in our former paper current intensity.

²⁾ Compare Equation 3, p. 382, These Proc. XXIII, No. 2 and 3, 1920.

³⁾ Compare Equation 1, p. 382, loc. cit.

^{*} These equations have been obtained from the Equations 1 and 3, p. 382, These Proc. XXIII, 2 and 3, after multiplication by $1/p$. This has been done on the strength of what was said in footnote 3, p. 385 of our paper of 1920.

$$\Delta p = j Ag \frac{l}{D} \sqrt{M} \dots \dots \dots (IV)$$

in which equation III must be valid for tubes the diameter of which is large with respect to the free path of the corpuscles, which is actually the case in RÜTTENAUER'S experiments. It is seen that equation III is identical with RÜTTENAUER'S empirical approximative formula.

§ 4. *On the influence of the potential gradient on the pressure effect.*

The "empirical" introduction of the potential gradient by RÜTTENAUER in the pressure effect equation rests on the testing by three kinds of observations:

a. the dependence of the observed values of the pressure effect on the potential gradient with one and the same current tube and the same gas with different current densities.

b. the dependence when the diameter of the discharging tube is varied;

c. the dependence when the nature of the gas is changed.

With reference to *a* we must remark that a critical consideration of the values published by RÜTTENAUER shows that the variation of the gradient is irregular, and besides smaller than the deviation of the values found for $\frac{p \Delta p}{Ag.l \sqrt{M}}$ interse, which values should be approximately constant. Thus in table 4 p. 272 of RÜTTENAUER'S publication the gradient for argon varies e.g. between 1,87 and 2,36, while the "constant value" $\frac{p \Delta p}{Ag.l \sqrt{M}}$ as a maximum varies between 3,70 and 4,98. For the rest the uncertainty in the determinations of the gradient seems to have been considerable. Where in our Thesis the gradient decreased with increase of current density, it appears to increase in a slight degree in the investigations recorded by RÜTTENAUER in table 3, whereas it decreased in a great degree in table 5. For this category of cases a constant value had, therefore, better be substituted for *g*, and the empirical formula becomes identical with our theoretical equation (I).

This is, therefore, in harmony with the statement expressed in our former publication (loc. cit. p. 390) that "in the case that the nature of the bearers is not modified" (hence for a definite gas) and "with not greatly varying tension" (potential gradient) *a* is a constant.

With reference to case *b* we remark that the experimentally determined influence of *g* is unmistakable. So far as the consequences of

g for a definite gas are concerned, this influence is also theoretically comprehensible. It already follows directly from the equation (4) of our former communication (I loc. cit. p. 384) which is based on the equation of motion of the electrically charged particles in the electric field, and from which appears the proportionality with the potential gradient V , provided the nature of the bearers undergo no change with V .

Already for this reason we may express this also in the equation of the mass-transportation by the electric current:

$$\text{mass-transportation} = \frac{1}{a} Q \cdot A \cdot \frac{760}{p} \cdot 2,32 \cdot 10^{-4} \text{ } ^1)$$

(equation (9) communication I), by replacing $\frac{1}{a}$ there by a factor bg , in which b is a constant for a definite gas. Hence $\frac{1}{a \cdot g} = b$ or $ag = \text{constant}$.

Let us also try to derive this directly from the nature of the electric conduction, and at the same time ascertain from it whether or no b has the same value for different gases. We then remind the reader that equation (9) of communication I teaches us that the pressure effect must be proportional to the part $\frac{1}{a}$ of the conduction, which takes place through ions charged with mass. This part is in direct ratio to the concentration of the ponderable ions. The problem may, therefore, be reduced to the question whether increase of g can cause increase of the concentration of the ions. In case of proportionality the equation $ag = \text{constant}$ may then be applied. *)

This relation will actually have validity for electropositive and noble gases, when J. FRANCK and G. HERTZ's ²⁾ elementary theory is adopted, according to which, as is known, perfectly elastic collisions between electron and atoms are assumed to take place, till — under influence of the electric field — the electron has passed over such a distance, and in this has obtained so much energy that its energy exceeds the value connected with the ionisation tension. The greater g , the shorter the time in which this value is obtained; the

¹⁾ With regard to the factor Q in the numerator, see note 1, p. 465.

*) We neglect the electrons liberated at the formation of the positive ions, supposing that within stationary conditions as many of these electrons are disappearing by recombination and formation of negative ions charged with mass. Additionally it may be remarked, that in the field of this investigation the number of ions compared with the number of free electrons is very small.

We intend to deal within short time more fully with this part of the subject.

²⁾ J. FRANCK and G. HERTZ. Verh. d. D. phys. Ges. 18, 213 ('16).

number of ionisations per time-unit will be directly proportional to g .

Later FRANCK and HERTZ¹⁾, just as C. D. CHILD²⁾, in connection with N. BOHR's theory have assumed that unelastic collision can also already take place before the tension of ionisation has been reached, in which then removal of one of the electrons of the atom to a path lying more outward, takes place. On return to the normal path this energy can then be emitted. Yet the result of the elementary theory will be approximated by three cases:

I. Through absorption of the radiated energy by neighbouring atoms (COMPTON³⁾).

II. By increase according in quanta of the energy of slow electrons on collision with dislocated atoms ("collisions of the second kind" in the theory of O. KLEIN and S. ROSSELAND; cf. also § 5).

III. (In a slight degree) through the renewed collision between dislocated atom and (rapid) electron, before the former has lost energy by radiation (K. J. VAN DER BIJL⁴⁾).

In agreement with our conclusion from equation (4) communication I it may therefore really be expected that in approximation the relation $a \cdot g = \text{const.}$ will hold for each of these gases separately, so long as the nature of the bearers is not subjected to any characteristic modification. For in this case the energy-compensation ensuing from I—III will always be the same percentage. This compensation must, however, be very different for different gases. So that, the tensions of ionisation also being so greatly divergent, we are led to accept the obvious conclusion that the value of ag will be different for different (noble) gases. We shall revert to this when discussing c .

That for the rest deviation is to be empirically observed *ad b* between a calculation based on formula III and observation (chiefly as a consequence of errors of observation), may appear from the following example (argon); though formula III would lead us to expect that the value:

$$\frac{Q \cdot p \cdot \Delta p}{Ag \sqrt{Ml}} \cdot 10^6$$

would be constant, a consideration of the values published by RÜTTENAUER shows that in table 5 e.g. the "constant" which amounts to about $2,3 \cdot 10^{-5}$, for one and the same noble gas in a definite case (in which the pressure varies from 0,5 to 0,64 mm., the current density from 1,49 to 1,21 A/cm². and the *bore of the tube from*

¹⁾ J. FRANCK and G. HERTZ. Phys. Zeitschr. **20**, 133 ('19).

²⁾ C. D. CHILD. Phil. Mag. (6) 278 ('14). Phys. Rev. (2) **15**, 33 ('20).

³⁾ K. T. COMPTON. Phys. Review (2) **15**, 476, 1920.

⁴⁾ K. J. VAN DER BIJL. Phys. Rev. **10**, 546 ('17).

place the values of Δp , A , and p found for neon (RÜTTENAUER, table 1 of his publication) in his table 4, we can write $g=5$ for neon, g being put at 2,0 for argon. Then we find:

TABLE A.

| Tube | | p | Ap | A | g | $\frac{p Ap}{Ag^2 \sqrt{Ml}} \cdot 10^5 = \text{constant}$ |
|--------------|--------|-------|-------|------|------|--|
| III $l = 60$ | Neon | 0.776 | 0.026 | 1.13 | 5. | 1.33 |
| III $l = 60$ | Argon | 0.741 | 0.062 | 1.21 | 2.0 | 4.98 |
| III $l = 60$ | Helium | 0.785 | 0.079 | 1.13 | 9.67 | 4.73 |

in other words the value of the "constant" is from 300 to 400%, higher for argon and helium than for neon. This shows in our opinion that it is unjustifiable to put the pressure effects for different gases comparable on such a basis.

Conclusion. It is necessary to replace RÜTTENAUER's empirical formula by the theoretical formula:

$$\Delta p = f \frac{A \sqrt{M} l}{D^3} \cdot q(g) \quad \text{resp.} \quad \Delta p = f \frac{A \sqrt{M} l}{p D^3} \cdot q(g)$$

in which $q(g)$ represents a function of the tension gradient, which in definite regions can approximately assume the form bg , in which b represents a constant the value of which is not the same for different gases.

§ 5. *Region of validity.*

We pointed in our previous communication that the phenomena in the path of the current are very complicated, and that our formulae are drawn up for more or less idealized cases. What makes A. RÜTTENAUER's determinations also so interesting is that they were carried out with noble gases, in which the conditions in the path of the current are naturally much less complicated than in the multi-atomic not-noble gases. Besides this investigator used a very long and wide positive pile, which brings out the influence of what happens in the positive pile better.

We mentioned already that in his second publication F. SKAUPY

then the ratio appears to agree with that which ensues from the values of the potential gradient as they have been measured by A. RÜTTENAUER with the positive pile.

as appears from some remarks, was inclined to the belief that the pressure effect might be referred to the phenomena of electrostriction. On page 215 loc.cit. it says about this: „In meiner schon erwähnten Arbeit über die Druckdifferenzen wurde gezeigt, dass bei Argonröhren innerhalb eines gewissen Druckgebietes (etwa 0,5 bis 3 mm. Hg) die sich bei einer gegebenen Stromstärke einstellende Druckdifferenz zwischen den Enden der 600 mm. langen, 0,8 cm. weiten Röhre umgekehrt proportional dem in der Röhre herrschenden Druck war. Durch einen Irrtum wurde diese Beziehung für alle Edelgase als gültig angenommen und darauf eine Theorie der Erscheinung gegründet. Diese kann wohl nicht richtig sein, da die Beziehung nur für Argon in dem genannten Druckgebiet erfüllt ist, aber nicht z. B. für Neon oder Helium.“

We point out, however, that A. RÜTTENAUER does not only find the dependence on p for argon, but also for the noble gases neon and helium, so that here no argument is present to induce us to look for the central point of the explanation of the phenomena in another region. We also remarked before that already in 1880 D. Bos¹⁾ showed that the effects which can ensue from the electrostriction for gases, are exceedingly small.

Besides, as we could show that the region covered by A. RÜTTENAUER quantitatively continued that examined by us, if only the right laws of diffusion are applied for every region, the validity of our theoretical conception is confirmed for investigations in which

TABLE B.

| | | | | | | | | | |
|--------------|----|------|----|------|----|-----|---|----|------------------|
| $\Delta p/p$ | as | 1.3 | to | 50 | or | ca. | 1 | to | 40 |
| Q | | 0.03 | to | 2 | or | ca. | 1 | to | 70 |
| p | | 0.15 | to | 1.2 | or | ca. | 1 | to | 8 |
| A | | 0.66 | to | 12.7 | or | ca. | 1 | to | 20 |
| g | | 0.6 | to | 45 | or | ca. | 1 | to | 75 ²⁾ |
| M | | 4 | to | 40 | or | ca. | 1 | to | 10 |
| l | | 5 | to | 60 | or | ca. | 1 | to | 12 |

¹⁾ Diss. Groningen.

²⁾ That for the tension gradient in this record of the ratios also observations made on nitrogen, are included, may be justified thus. We published the following measurements already before: $p_1 = 1.18$ m.m. Hg. Terminal voltage 288 V. $l_1 = 6.5$ c.m. $q_1 = 3.15$ m.m.². $M_1 = 28$, $A_1 = 12.7$ Amp. c.m.². $p_1 = 0.18$ m.m. $p_2 = 0.15$, $l_2 = 5$, $q_2 = 3.15$, $M_2 = 28$, $A_2 = 12.7$. For nitrogen in uviole glass with $Q = 3.15$ m.m.² there are known to the author (Table C) the following three observations of p in connection with the terminal voltage, from which we arrive at the bracketed values for the potential difference between the ends of the positive pile

the values of the different quantities, are as a maximum to each other in the ratio as recorded in table B.

Continued experimental investigation on others than the examined gases but also on the latter themselves can, however, still reveal much. For all these investigations have been made within limits for which it may be assumed that the nature of the luminescent centres and of the current-conducting ions does not undergo any essential change. We pointed out before that it follows from the researches of J. STARK¹⁾, A. WEHNELT and J. FRANCK²⁾ that when p is sufficiently reduced, and g sufficiently raised, the pressure-effect reverses its sign³⁾. It may, however, also be questioned, what happens, when the nature of the discharge is maintained, but the current-density is greatly increased. We know only one indication of an essential change taking place in this case; already in I we expressed⁴⁾ the desirability of examining by means of continued investigations of the pressure-effect, whether anything could be derived from this

[by making by estimation, an approximate calculation of the cathode and anode gradient and the loss of potential between the electrodes and the entrances of

TABLE C.

| p in m.m. Hg | Terminal voltage | Pot. diff. pos. column | Thesis |
|----------------|------------------|------------------------|---------|
| 0.34 | 212 Volt | (ca. 170 Volt) | table 4 |
| 1.19 | 288 " | (ca. 240 ") | " 10 |
| 2.38 | 350 " | (ca. 290 ") | " 14 |

the capillary path of the current]. Extrapolating we then find for $p = 0.15$: pot. gradient in the pos. pile: about 145 Volts. If in connection with this we assume the pot. gradient to be $\frac{5}{3}$ at 0.15 m.m. of that at $p_1 = 1.19$ m.m.

[hence $\frac{g_1}{g_2} = \frac{5}{3}$], and if we bear in mind that we must apply here the formula

$\Delta p = f Ag \frac{l}{D} \sqrt{M}$, the following formula would follow from this

$$\frac{\Delta p_1}{\Delta p_2} = \frac{g_1}{g_2} \cdot \frac{l_1}{l_2} = \frac{5}{3} \cdot \frac{6,5}{5} = 2,2$$

the ratio measured on nitrogen being $\frac{0,18}{0,08} = 2,3$.

More and more sharply defined measurements are very desirable also here.

¹⁾ J. STARK. BOLTZMANN-Festschrift 1904.

²⁾ A. WEHNELT and J. FRANCK. Verh. d. D. phys. Ges. 12, 444 (1910).

³⁾ For convenience sake we shall distinguish this as "negative" effect from the "positive" effect found by us.

⁴⁾ Communication I loc. cit. 1178.

about change of the luminescent centres on the transition from the blue to the red *argon*-spectrum. On this head A. RÜTTENAUER'S experiments give no decisive result, because the current-densities applied by this investigator, are too small. The author expresses the hope that — experimenting in this region being impossible to him for the present — this remark may induce others to undertake a further investigation.

§ 6. *Quantitative and Simultaneous Parallelism of Light Emission and Pressure Effect.*

We derived in our former publication that the pressure-effects are chiefly due to the transportation of ions by the electric current (mass-transportation), *which ions have originated at the impact between electrons and atoms.* Where the extension of the experiments corroborates our theoretical conception quantitatively, we think that it is not devoid of interest to remark here that the theory of quanta manifests its simultaneous and quantitative validity with respect to light emission and pressure effect by means of the positive pile.

We have, indeed, to do here with two typical regions of the application of the theory of quanta:

1. With light emission, the region of spectroscopy, in which the phenomena should be studied, which present themselves on the *return* of electrons from abnormal to less abnormal paths;

2. With the region of the pressure effects in which the collisions should be studied between electrons and atoms, the formation of ions, hence*) the passing of the atom-electrons *from* normal to abnormal paths.

As soon as the "bearers" change their character, both the character of the light emission and of the pressure effect changes. The latter may reverse its sign; as regards the light emission the change finds among others a pregnant expression in the law of displacement already cited in our previous paper.

If on the other hand the electric conditions do not change characteristically, if the bearers continue to preserve the same character, our quantitative objective measurements of the light emission and our and RÜTTENAUER'S manometric determinations of the pressure effect prove the *simultaneous quantitative proportionality of light- and pressure effect with the added energy.* That the light emission does not change its character through increase of the added *quantity* of energy, was only what was to be expected according to the theory of quanta. Accordingly we consider particularly the fact that the same thing holds simultaneously for the pressure-effect, a contribution

*) As far as the positive ions are concerned.

to our knowledge. We see in this a confirmation of the view that the *atoms both absorb and emit energy in quanta*, at the same time an *interaction* between the two regions, which latter finds expression in a related region of investigation, among others in KLEIN and ROSSELAND's theory¹⁾.

The well-known theoretical parallelism between these two regions and the simultaneous parallelism between the observations on the pressure effects and the light emission which have now been experimentally shown *objectively*, corroborate anew the close relation, the *unity between these two classes of phenomena*.

§ 7. Summary.

1. Our priority with regard to the "positive" pressure effect is established.

It is shown that A. RÜTTENAUER's experimental investigations quantitatively confirm the theoretical view and formulae about the pressure effect found by us, which we gave before. This establishes confirms for an extensive region of validity defined in § 5 that the *pressure differences chiefly occur in consequence of mass-transportation by the electric current*.

2. It is desirable to replace the empirical formula given by A. RÜTTENAUER for the pressure effect by two formulae derivable from the theory, dependent on the ratio between the free path of the corpuseles and the (round) diameter of the tube, viz.:

$$\Delta p = f \frac{A \sqrt{Ml}}{D^3} \cdot \varphi(g) \quad \text{resp.} \quad \Delta p = f \frac{A \sqrt{Ml}}{p D^4} \cdot \varphi(g)$$

in which $\varphi(g)$ represents a function of the potential gradient, which can assume approximately the form bg in definite regions; in which b represents a constant the value of which is *different* for different gases.

3. It is shown that the opinion advanced by F. SKAUPY that the pressure effect would be determined by the elastic electron impact, is untenable.

4. The significance of the simultaneous parallelism of the quantitatively and objectively measured light and pressure effects with regard to the theory of the quanta is pointed out. It confirms that the atoms both emit and absorb energy in quanta.

5. Attention is drawn to the desirability of extending the investigations, in particular also to argon.

Dordrecht, October 11, 1922.

¹⁾ KLEIN en ROSSELAND. Zeitschr. f. Physik. 4, 46 ('21).

Botany. — “*On a new clinostat after DE BOUTER*”. By Prof.
F. A. F. C. WENT.

(Communicated at the meeting of December 30, 1922).

It has been known to every botanist for more than 15 years, that the clinostats in present use are not satisfactory with regard to great precision. Already in 1907 VAN HARREVELD¹⁾ made the errors of those instruments known to us in a detailed study. He himself constructed a much better clinostat, satisfying high requirements, but nevertheless introduced only in a few laboratories. This will be chiefly due to the great costs, unsurmountable for most laboratories.

To the above fact it has been chiefly due, that Mr. P. A. DE BOUTER, mechanic of the Botanical Laboratory at Utrecht, asked himself, whether it would not be possible to construct a much cheaper clinostat, nevertheless coming up to high requirements. Those considerations have led to the construction of a new clinostat, the description of which follows.

Fig. 1 shows the clinostat in a more or less schematic way. 1 is a shuntmotor, running directly full speed, and connected by a belt 3, with a flywheel 2, to the axis of which a pinion has been fixed. With the aid of cog-wheels its motion is transmitted to the proper clinostat 5. The axis of the fly-wheel turns on ball-bearings. Now the question is, to make this fly-wheel revolve exactly once a second; this cannot be attained by altering the speed of the motor or by regulating the diameter of the grooved wheels because of a too great oscillation of the voltage of the town-plant. Neither does the motor run regularly with equal voltage; namely with excentric load. For this reason a different construction has been used here.

Into the circuit + — of the motor a resistance 12 has been inserted in the form of a lamp, in consequence of which the fly-wheel runs a little too slowly, e.g. half a rotation a second. If however this resistance is put out of circuit, the fly-wheel revolves a little too fast, e.g. two rotations a second. This putting out takes

¹⁾ PH. VAN HARREVELD, Die Unzulänglichkeit der heutigen Klinostaten für reiz-physiologische Untersuchungen. Recueil des Travaux botaniques néerlandais. III. 1907, p. 173.

place every second with the aid of the pendulum of a clock keeping exact time.

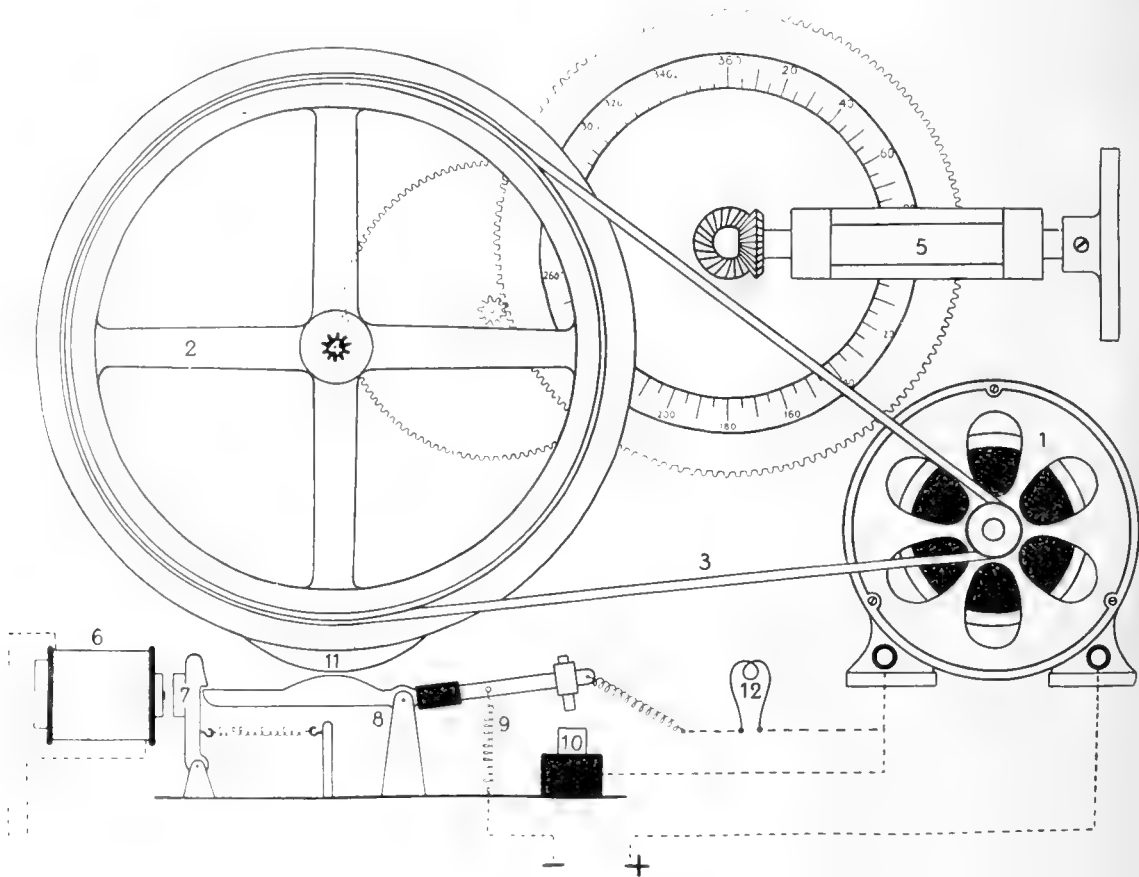


Fig. 1. Sketch of the new clinostat; description in the text.

At 6 we see an electro-magnet every second turning magnetic for an instant and attracting the spring-armature 7. The turning-over switch 8 is drawn to one side by the spring 9, in consequence of which the contact 10 is made. The current passes from + through the motor straight to contact 10, next through a part of the switch 8, through the spring 9 and finally to —; in this way the motor runs full speed.

But on the fly-wheel a cam 11 has been fixed; this makes the switch 8 catch behind the armature 7, in consequence of which the circuit is broken at 10. Then the current has to pass through the resistance and the motor runs slower.

The final result is that the fly-wheel makes exactly one revolution a second. Even considerable oscillations of the voltage of the light

and power-station are of no consequence, the only result will be, that the cam 11 is a little more to the right or to the left at the moment, at which the second circuit is closed, so that only the ratio of the rapidly and slowly revolving parts of the axis of the fly-wheel may be altered every second. This is of no importance, because the axis of the clinostat revolves at a much slower rate and the movement is transmitted to this by means of the cog-wheels 4, etc.

To the horizontal axis of the clinostat a conical cog-wheel has been fixed, in which another conical cog-wheel catches, fastened to an adjustable axis 5. This latter axis has been fitted on in such a way, that it can revolve on the horizontal axis and can be fixed, while the rotatory movement is not impeded. This enables us to give the axis of the clinostat any desirable position. By fixing the adjustable axis and releasing the adjusting-apparatus, a rotation of the plant perpendicular to the horizontal axis may be obtained. This arrangement is shown in fig. 2; the adjustable axis is fastened with the screw *A*, the adjusting-apparatus with the handle *B*.

Fig. 3 gives a backview of the whole apparatus, in which the arrangement of fig. 2 has not yet been fitted on. This figure shows, that the apparatus is comparatively small and may easily be removed by one person. The position of the axis too may be modified without any difficulty during the experiment.

To the simple construction it is owing that the costs of purchase are considerably lower than of any other satisfactory clinostat. An objection is, that the motor keeps running throughout the experiment and therefore constantly uses current. But then the axis revolves with great power, so that considerable weights can be carried, while excentric loading that is rather considerable, does not cause any alteration in the regular running of the clinostat.

In order to check the running of this clinostat and compare it with PFEFFER'S and VAN HARREVELD'S clinostats, the recording-apparatus of the auxanometer of KONINGSBERGER¹⁾ was used.

For this purpose electrodes were fixed to the axis of the clinostat either right opposite to each other or at an angle of 90°, in such a way, that after each full rotation of the axis, the top of such an electrode once made contact in a mercurydish and in this way a circuit was closed for a short moment. Closing that circuit caused a writing glass-pen to be stopped in its course and to be

¹⁾ V. J. KONINGSBERGER, A method of recording growth under various external influences. Proceedings Kon. Ak. v. Wet. Amsterdam. W. en Nat. Afd. XXX, 6/7. 1921.

sent back to its starting-point, while a drum with paper, on which the recording occurred, was moved on 1.5 mm.

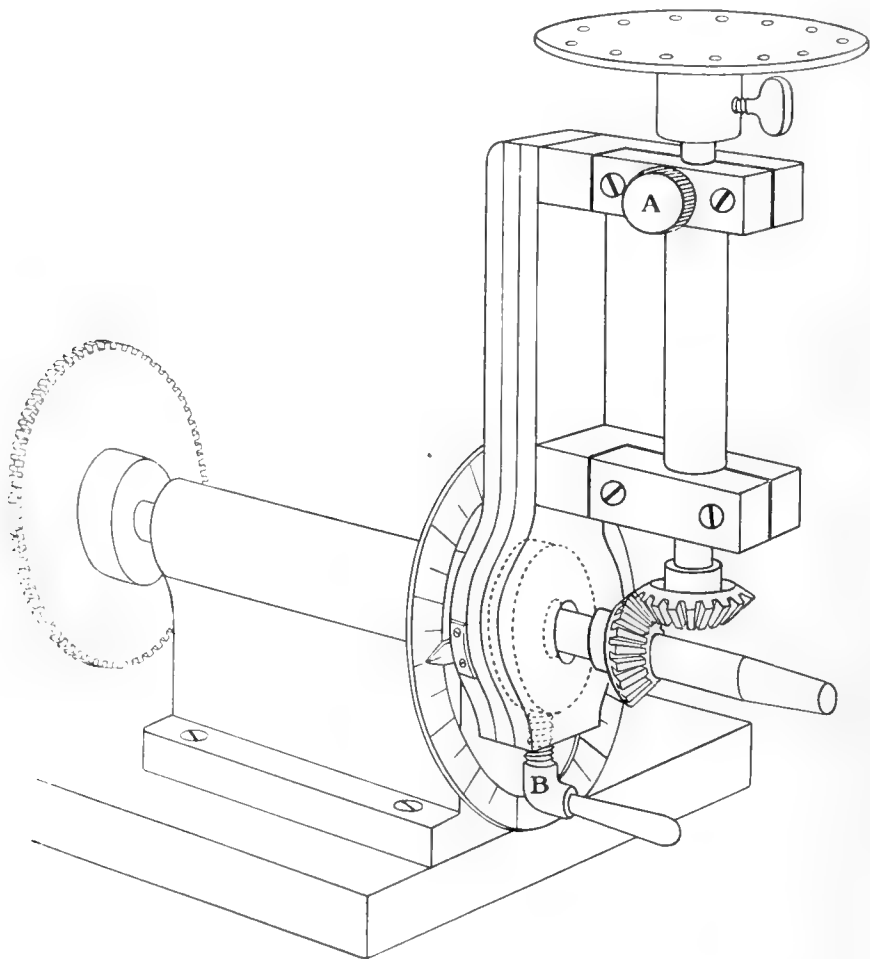


Fig. 2. Top of the clinostat-axis with conical wheels, as described in the text.

The pen moves along the paper with a velocity of 1 mm. a second, writing a straight line. A number of parallel lines arises in this way, as shown in fig. 4, drawn for so many seconds as the period amounts to, needed by the clinostat-axis to make a half or a quarter of a rotation.

If therefore the clinostat runs regularly, these lines must be of equal length, or may differ one second at most, with respect to the point of time at which the contact with the mercury is made.

In the figure something else has been recorded: every 6 minutes

a time-signal is given on a continuous line T. Of course the distance covered by the circumference of the clinostat-axis in successive 6

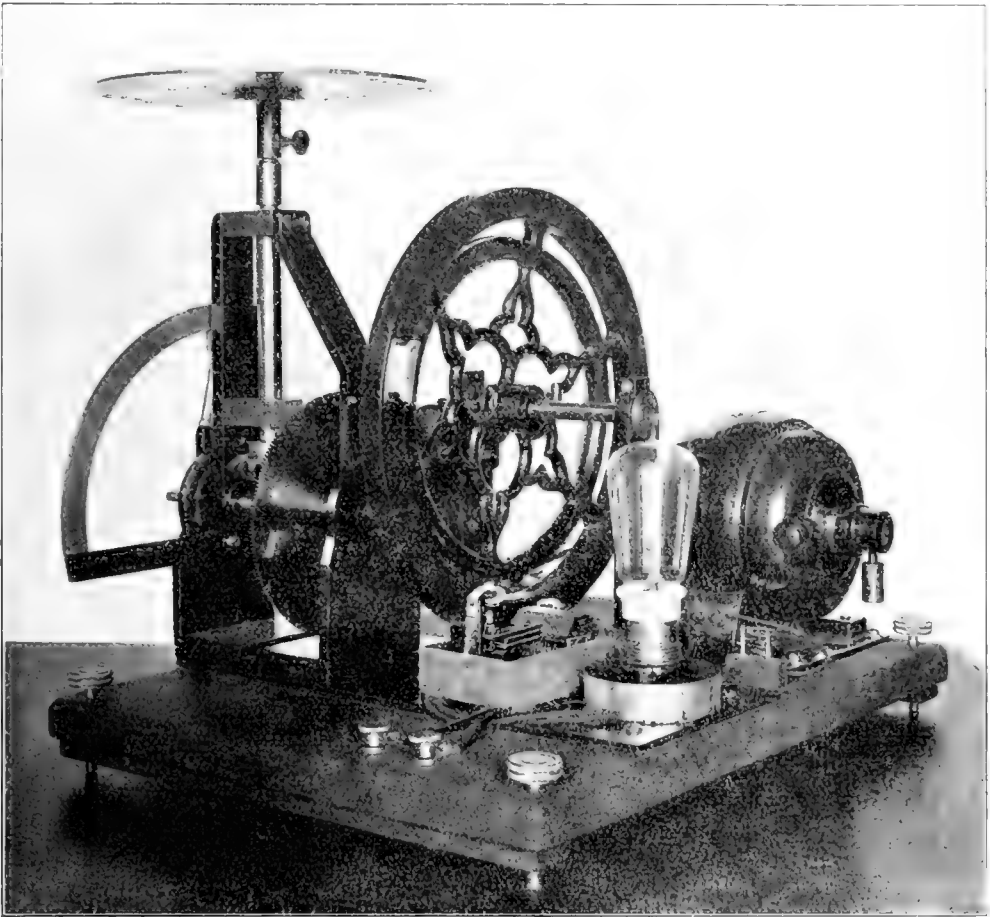


Fig. 3. Backview of the whole clinostat.

minutes must always be the same; so the distance between the time-signals must not vary with a good clinostat.

Now the various clinostats were tested in two ways; partly without load, partly with an excentric load on the axis. This latter was done, because that very unequal load causes the greatest difficulties in practice, especially when in the dark plants have to be fixed on a clinostat, or when we have to try several times in order to get an exact centering, when meanwhile the plants have already been exposed to the unilateral influence of gravitation for a long time. Fig. 4 shows the results of those experiments.

In I the behaviour of a clinostat of PFEFFER is shown with an excentric load, amounting to 0,26 KG. when calculated on the axis.

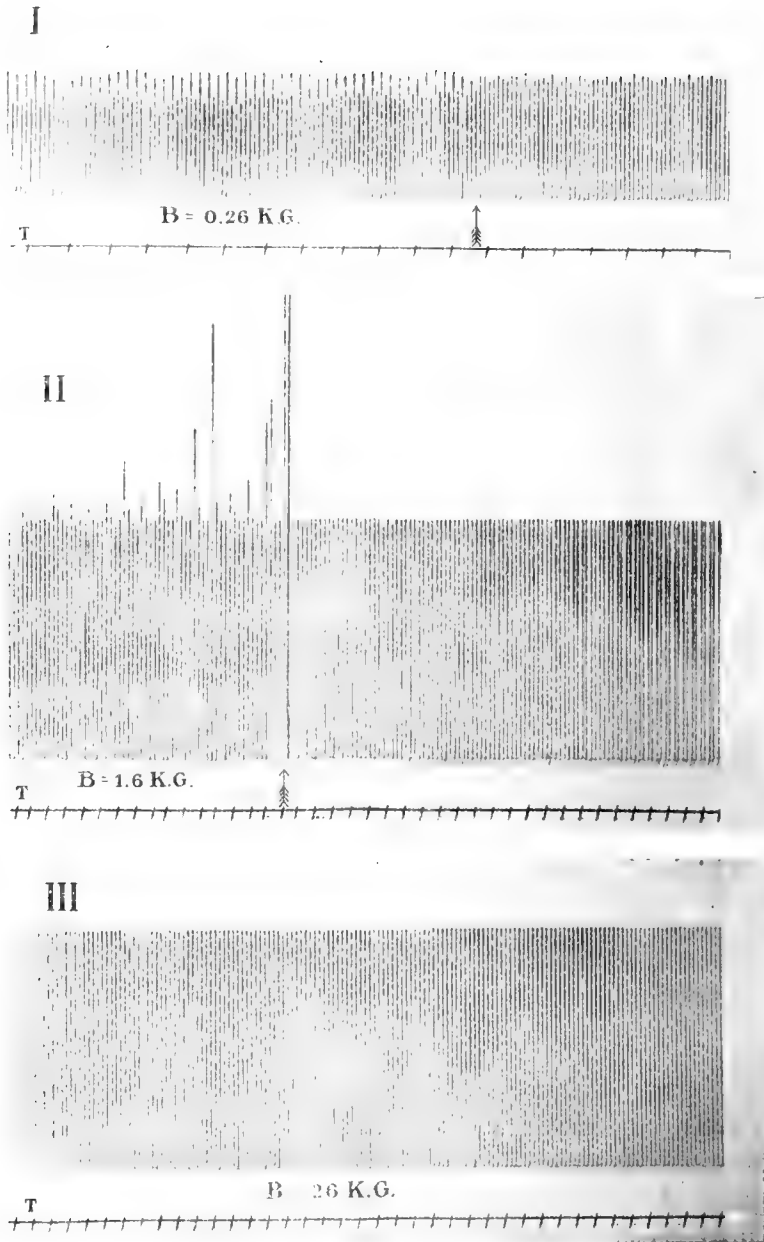


Fig. 4. I. Clinostat of PFEFFER. Records of half rotations.

B is the excentric overload converted on the axis. At \uparrow this load was removed. II. Clinostat of VAN HARREVELD. Record of $1/4$ rotations. B as above. At \uparrow this load was increased to 2 KG. at which the clinostat stopped; next the overload was removed. III. Clinostat of DE BOUTER. Record of half rotations. B. excentric overload as above. In all 3 figures T is the time-line, checked every 6 minutes.

It may be noticed how great the difference is between the two halves of the revolution, while this difference disappears beyond the arrow, indicating the moment at which the excentric load is removed.

II refers to the clinostat of VAN HARREVELD; here the excentric load was larger, 1.6 KG., calculated on the axis and there too irregularities appear, which are sometimes very considerable. The arrow indicates the moment at which the excentric load was increased to 2 KG. The clinostat had come to a stop; this happened with a clock-weight of 13 KG. If a heavier weight had been chosen, the movement would of course have continued. After removing every excentric load, the running was perfectly regular, as appears from the rest of the figure.

III shows the working of the clinostat DE BOUTER with an excentric load of 26 KG. calculated on the axis. We see that notwithstanding this, it runs quite regularly, so that the superiority of this clinostat is perfectly clear from the figure.

A contemplation of the time-signals T in the three parts of the figure will necessarily lead to the same conclusion; these time-signals gave a sign after every six minutes.

Summarizing I arrive at the conclusion, that this clinostat is a great improvement on those hitherto used. Now that plant-physiology is developing more and more into an exact science, the old "à peu près" methods will have to be left and therefore care should be taken that the instruments used come up to high requirements of precision.

Utrecht, Botanical Laboratory, December 1922.

Biochemistry. - „*Concerning the Synthetic Action of Bacteria in the Paunch of the Cow*”. By Prof. B. SJOLLEMA and J. E. VAN DER ZANDE. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated at the meeting of December 30, 1922).

The question whether bacterial processes occurring in the paunch of ruminants are significant for the metabolism of these animals¹⁾, should be given more attention to than here to fore, since, by way of trial, ruminants are fed with urea, made from the nitrogen in the air. For the significance of the substitution of urea for protein in the animal's diet depends to a great extent on the capacity of the bacteria of the paunch to synthesize from urea, in the presence of non-nitrogenous substances, the amino-acids which the higher animals are not able to build up.

Tryptophane is one of the amino-acids indispensable to man and to the higher animals. It is highly improbable that mammals can synthesize tyrosine from non-aromatic substances.

We have tried to ascertain whether these two substances can be built up by the bacteria occurring in the cow's paunch, when, beyond ammonia no other source of nitrogen is present than urea, asparagin or aspartic acid.

Our procedure was as follows:²⁾

Directly when the animal was killed, part of the contents of the paunch was brought to our Laboratory in a sterile bottle, fitted with a glass stopper³⁾.

With the help of a sterile wire a little of the paunch contents (i.e. of the turbid fluid after removal of the coarser particles) was transmitted to sterile nutrient solutions, contained in Erlenmeyer-flasks plugged with cotton-wool, and which were of a depth of 1

¹⁾ Here we refer to the development of volatile acids in the paunch from sugar, as demonstrated before by one of us (B. S.). See Bericht III 5th International. Congres für "angewandte Chemie" Berlin 1903, p. 825.

²⁾ It was adopted because bacterial growth could not easily be recognized directly in the turbid juice of the paunch (even when much diluted), and also because we wanted quantitative data regarding tryptophane-formation.

³⁾ We would here gratefully acknowledge our thanks to Mr. HOEFNAGEL and to Mr. DE GRAAF, respectively director and sub-director of the Utrecht abattoir, for their kind assistance in obtaining the material required for these experiments.

to 1½, cm. The flasks were then left standing in an incubator at 36° C. Duplicate cultures were made for each experiment.

When the bacteria were fairly developed (which was the case after two days) one of the cultures was examined for the presence of the amino-acids, alluded to above; the other remained in the incubator. Moreover a new culture-medium was inoculated with it. We used USCHINSKY's solution, unmodified or modified as indicated below.¹⁾

Since the p_H of the paunch contents was about 7.4, we took care to let the p_H of our culture media be the same.

In order to demonstrate the presence of tryptophane we applied the reactions of VOISENET (with HCl, formaldehyde and nitrite) and of HOPKINS-COLE (with H₂SO₄ and glyoxylic acid). MILLON's reagent was used for ascertaining the presence of tyrosine. VOISENET's reagent stains differently with indole and with tryptophane. Indole after shaking out with ether was reacted on with dimethylpara amidobenzaldehyde.

USCHINSKI's solution, whether modified or not, but invariably without an aromatic or heterocyclic compound, inoculated with a small quantum of the paunch-contents, always gave in the sediment (obtained by centrifugation after the addition of alcohol) after a sojourn at 36° C. in an incubator, a very distinct tryptophane, and tyrosine-reaction, whereas initially the reactions were negative.

A better growth and more powerful reactions were obtained by mixing 10 c.c. of the fresh paunch fluid with 25 c.c. of USCHINSKI's solution.

Whereas the reactions in the sediment were invariably positive, the supernatant fluid displayed negative reactions.

In order to make sure that the tryptophane and the tyrosine reactions were not due to other indole or phenol-derivatives, the sediment was, in a few cases, centrifuged anew with diluted alcohol and once more with ether (indole). The reactions of the sediment were as distinct as before. The cultures themselves were also shaken out with ether some times. With the above-named aromatic aldehyde the ether gave a negative indole-reaction. It was evident, therefore, that neither free tryptophane, nor other free indole-derivatives, nor free phenol-like bodies were present. The positive reactions may, therefore, be attributed to the body-protein of the bacteria.

On inoculation of new USCHINSKY solutions with the cultures an

¹⁾ The ordinary USCHINSKY-solution contains K, Na, Ca, Mg, PO₄, Cl and SO₄; besides glycerol, ammonium-lactate and sodium aspartate.

excellent growth could be noted, and after a couple of days positive tryptophane, and tyrosine-reactions of the sediment.

The present investigation, therefore, shows clearly that there are bacteria in the paunch of the cow, capable of building up tryptophane and tyrosine with an aliphatic nitrogen-compound and with ammonia. With every one of the six paunches we succeeded in obtaining this result.

We consider the presence of tyrosine to be established when bacterial bodies show a phenol-reaction (MILLON'S). The non-specificity of the tryptophane reactions is of no importance in our experiments. They are only needed to show the presence of an indole-derivative so long as tryptophane is considered as sole indole-derivative in the protein-molecule¹⁾.

Positive results were also obtained in the experiments in which asparagin (or sodium-aspartate) had been replaced by urea. The bacterial growth was, however, decidedly slower. The ammonium-lactate had been substituted in these experiments by potassium lactate, so that urea was the sole source of nitrogen.

After 2×24 hours the tryptophane-reactions were as a rule weak in the turbid culture solution and very clear in the sediment, which had been obtained through centrifugation.

A couple of times we added tryptophane to the USCHINSKY solution which resulted in the formation of indole contrary to the other experiments.

Direct addition of indole inhibited bacterial growth considerably; it was arrested completely by 50 mgms per 100 c.c.

Whether tryptophane can be developed from indole, as assumed by LOGIE, is not borne out by the present experiments, for, where addition of a small quantity of indole caused some bacterial growth, the formation of tryptophane may have resulted from the presence of ammonium-nitrogen or asparagine-nitrogen.

When substituting glucose for the glycerol and the lactic acid of the USCHINSKY-solution a tryptophane synthesis takes place which is almost equal to that in the ordinary USCHINSKY-solution.

In experiments under approximately anaërobic conditions the growth was inferior to that obtained in the manner above-described. An experiment, in which air was drawn through the fluid by suction, did not yield a larger growth than usual.

¹⁾ Since gelatine does not yield VOISENET'S, nor MILLON'S reaction and proline and oxyproline are contained in it, it follows that these two amino-acids do not give these reactions.

The histidine reactions thus far obtained, were still somewhat doubtful.

Several microscopic preparations were made of the cultures. Sometimes different species were present, i.e. diplococci, rod-shaped bacteria; sometimes staphylococci and streptococci; in one case the predominance of one species was such as to render it difficult to find another. These almost pure cultures were not always made up of the same bacteria; sometimes they were small ovoid, at other times rod-shaped bacteria.

It being known that even various stocks of one and the same species may differ largely as to the chemical changes they engender, we did not ascertain whether the developing species were in any way concerned in the result of the reaction.

According to an approximate quantitative determination in a culture, three days old, the sediment of 100 cc. contained about 3 mgms of tryptophane, i.e. per Liter 30 mgms, or 3 grms per 100 L. (putting the paunch contents at 100 L.).

A man of 70 k.g. weight requires per day about $2\frac{1}{2}$ —3 grms of tryptophane. Assuming the same ratio for a cow, this animal would require per day about $17\frac{1}{2}$ —20 grms. The quantity necessary for the production of milk has not been taken into account here.

Putting the tryptophane content of milk per L. at about 750 mgms, and putting the daily flow of milk at, say, 12 Liters, the animal would have to take in another quantum of 9 grms of tryptophane.

As far as we are aware tryptophane synthesis by bacteria (*B. coli* and *B. FRIEDLÄNDER*) from ammoniac and aliphatic nitrogen-compounds, has been demonstrated only once, viz. by LOGIE¹⁾.

From the publication of BRAUN and CAHN—BRONNER²⁾, which came to our notice when our experiments had nearly come to an end, it may be inferred that their experiments also pointed to tryptophane synthesis, for they could grow *coli*, paratyphoid-, and FRIEDLÄNDER-bacteria when ammonia nitrogen was the only source of nitrogen present. Where they report, that under perfectly anaërobic conditions ammoniac-assimilation is impossible, even after the supply of more energy, the question rises (granting their theory to hold generally) whether in the rumination process an aërobic condition exists which allows any synthesis worth mentioning.

It may rationally be supposed that, wherever micro-organisms manage to live on inorganic or aliphatic nitrogen-sources, they them-

¹⁾ J. of Pathol. and Bact. Bd. 23, 224 (1919/1920).

²⁾ Biochem. Zeitschrift Bd. 131, 272 (1922).

selves derive the cyclic amino-acids from these sources, it being a fact that protein, containing these amino-acids, is always present in these organisms.

In how far the amino-acids, formed in the paunch, are of use to the metabolism of ruminants, will have to be made out by food-experiments, which will also have to show whether the bacterial protein, formed in the paunch, is resorbed.

Let it be observed that we have never succeeded in demonstrating tryptophane (or tyrosine) in the fresh turbid paunch-fluid (after the removal of the solid particles) and also that we were not more successful in this respect after cultivating for some days in the incubator, either under aërobie or anaërobie conditions.

Meanwhile we should not omit stating that reactions in a fluid like the paunch-fluid, are far less sensitive than those in unstained solutions. Only when 7 mgms of tryptophane per 100 cc. was added in the form of protein (bloodplasma) a perfectly distinct tryptophane-reaction was recognizable.

Still, the phenomenon, just alluded to, does not point to an abundant tryptophane formation in the paunch, which is the more striking since the paunch fluid with USCHINSKY'S solution (10:25) yields negative results at starting, but exhibits distinct reactions after 2×24 hrs.

The above experiments show: 1°. that various bacteria present in the paunch of cows can build up the amino-acids tryptophane and tyrosine from ammonia nitrogen plus asparagine (or aspartic) nitrogen, and also from urea as nitrogen-source.

2°. that these bacteria can form quantities of tryptophane in the culture-medium of USCHINSKY, which may be of some significance for the metabolism in cows; however it is not quite certain whether this synthesis is equally intense in the paunch.

(From the Chem. Labor. of the Utrecht Veterinary Univ.)

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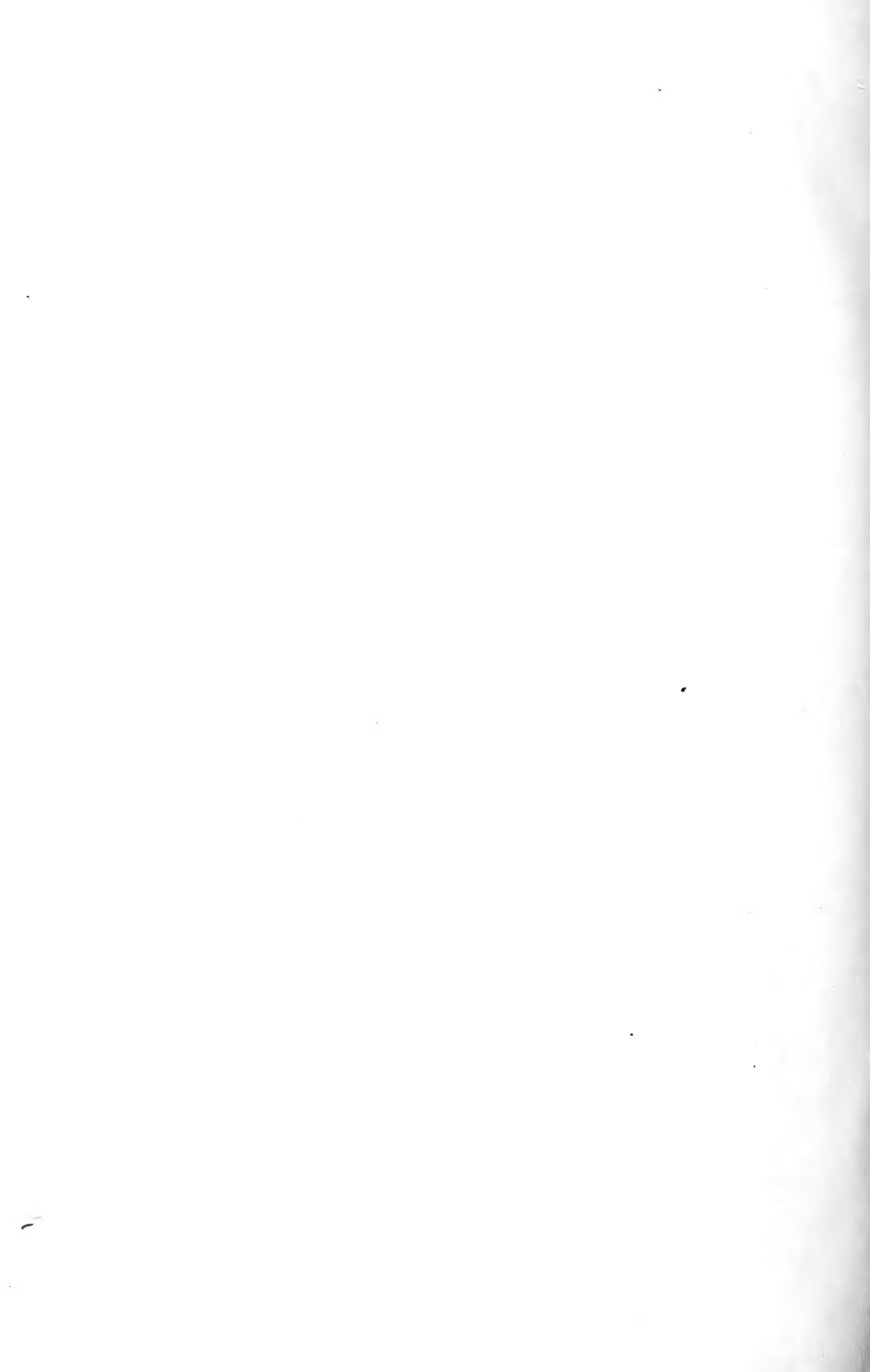
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